

PLATINUM-COPPER FUEL CELL CATALYST

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[0001] The present invention relates to compositions which are useful as catalysts in fuel cell electrodes (e.g., electrocatalysts) and other catalytic structures, and which comprise platinum and copper.

DESCRIPTION OF RELATED TECHNOLOGY

5 **[0002]** A fuel cell is an electrochemical device for directly converting the chemical energy generated from an oxidation-reduction reaction of a fuel such as hydrogen or hydrocarbon-based fuels and an oxidizer such as oxygen gas (in air) supplied thereto into a low-voltage direct current. Thus, fuel cells chemically combine the molecules of a fuel and an oxidizer without burning, dispensing with
10 the inefficiencies and pollution of traditional combustion.

[0003] A fuel cell is generally comprised of a fuel electrode (anode), an oxidizer electrode (cathode), an electrolyte interposed between the electrodes (alkaline or acidic), and means for separately supplying a stream of fuel and a stream of oxidizer to the anode and the cathode, respectively. In operation, fuel
15 supplied to the anode is oxidized, releasing electrons that are conducted via an external circuit to the cathode. At the cathode, the supplied electrons are consumed when the oxidizer is reduced. The current flowing through the external circuit can be made to do useful work.

[0004] There are several types of fuel cells, including those having
20 electrolytes of phosphoric acid, molten carbonate, solid oxide, potassium hydroxide, or a proton exchange membrane. A phosphoric acid fuel cell operates at about 160-220 °C, and preferably at about 190-200 °C. This type of fuel cell is currently being used for multi-megawatt utility power generation and for co-generation systems (i.e., combined heat and power generation) in the
25 to several hundred kilowatts range.

[0005] In contrast, proton exchange membrane fuel cells use a solid proton-conducting polymer membrane as the electrolyte. Typically, the polymer membrane is maintained in a hydrated form during operation in order to prevent loss of ionic conduction which limits the operation temperature typically to
30 between about 70 and about 120°C, depending on the operating pressure, and

preferably below about 100 °C. Proton exchange membrane fuel cells have a much higher power density than liquid electrolyte fuel cells (e.g., phosphoric acid), and can vary output quickly to meet shifts in power demand. Thus, they are suited for applications such as in automobiles and small-scale residential
5 power generation where quick startup is a consideration.

[0006] In some applications (e.g., automotive) pure hydrogen gas is the optimum fuel; however, in other applications where a lower operational cost is desirable, a reformed hydrogen-containing gas is an appropriate fuel. A reformed hydrogen-containing gas is produced, for example, by steam-reforming
10 methanol and water at 200-300 °C to a hydrogen-rich fuel gas containing carbon dioxide. Theoretically, the reformat gas consists of 75 vol% hydrogen and 25 vol% carbon dioxide. In practice, however, this gas also contains nitrogen, oxygen and, depending on the degree of purity, varying amounts of carbon monoxide (up to 1 vol%). Although some electronic devices also reform liquid
15 fuel to hydrogen, in some applications the conversion of a liquid fuel directly into electricity is desirable, as then high storage density and system simplicity are combined. In particular, methanol is an especially desirable fuel because it has a high energy density, a low cost, and is produced from renewable resources.

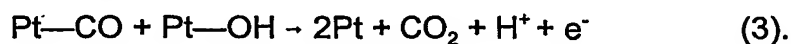
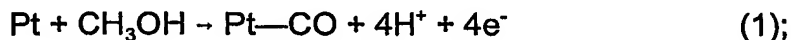
[0007] For the oxidation and reduction reactions in a fuel cell to proceed
20 at useful rates, especially at operating temperatures below about 300 °C, electrocatalyst materials are typically provided at the electrodes. Initially, fuel cells used electrocatalysts made of a single metal, usually platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), osmium (Os), silver (Ag) or gold (Au), because they are able to withstand the corrosive environment. In general,
25 platinum is considered to be the most efficient and stable single-metal electrocatalyst for fuel cells operating below about 300 °C.

[0008] While the above-noted elements were first used in fuel cells in metallic powder form, later techniques were developed to disperse these metals over the surface of electrically conductive supports (e.g., carbon black) to
30 increase the surface area of the electrocatalyst. An increase in the surface area of the electrocatalyst in turn increases the number of reactive sites, leading to improved efficiency of the cell. Nevertheless, fuel cell performance typically declines over time because the presence of electrolyte, high temperatures and molecular oxygen dissolve the electrocatalyst and/or sinter the dispersed
35 electrocatalyst by surface migration or dissolution/re-precipitation.

[0009] Although platinum is considered to be the most efficient and stable single-metal electrocatalyst for fuel cells, it is costly. Additionally, an increase in electrocatalyst activity over platinum is desirable, if not necessary,

for wide-scale commercialization of fuel cell technology. However, the development of cathode fuel cell electrocatalyst materials faces longstanding challenges. The greatest challenge is the improvement of the electrode kinetics of the oxygen reduction reaction. In fact, sluggish electrochemical reaction kinetics has prevented electrocatalysts from attaining the thermodynamic reversible electrode potential for oxygen reduction. This is reflected in exchange current densities of around 10^{-10} to 10^{-12} A/cm² for oxygen reduction on, for example, Pt at low and medium temperatures. A factor contributing to this phenomenon includes the fact that the desired reduction of oxygen to water is a four-electron transfer reaction and typically involves breaking a strong O-O bond early in the reaction. In addition, the open circuit voltage is lowered from the thermodynamic potential for oxygen reduction due to the formation of peroxide and possible platinum oxides that inhibit the reaction. A second challenge is the stability of the oxygen electrode (cathode) during long-term operation. Specifically, a fuel cell cathode operates in a regime in which even the most unreactive metals are not completely stable. Thus, alloy compositions that contain non-noble metal elements may have a rate of corrosion that would negatively impact the projected lifetime of a fuel cell. Corrosion may be more severe when the cell is operating near open circuit conditions - - the most desirable potential for thermodynamic efficiency.

[0010] Electrocatalyst materials at the anode also face challenges during fuel cell operation. Specifically, as the concentration of carbon monoxide (CO) rises above about 10 ppm in the fuel the surface of the electrocatalyst can be rapidly poisoned. As a result, platinum (by itself) is a poor electrocatalyst if the fuel stream contains carbon monoxide (e.g., reformed-hydrogen gas typically exceeds 100 ppm). Liquid hydrocarbon-based fuels (e.g., methanol) present an even greater poisoning problem. Specifically, the surface of the platinum becomes blocked with the adsorbed intermediate, carbon monoxide (CO). It has been reported that H₂O plays a key role in the removal of such poisoning species in accordance with the following reactions:



As indicated by the foregoing reactions, the methanol is adsorbed and partially oxidized by platinum on the surface of the electrode (1). Adsorbed OH, from the hydrolysis of water, reacts with the adsorbed CO to produce carbon dioxide and a proton (2,3). However, platinum does not form OH species rapidly at the potentials where fuel cell electrodes operate (e.g., 200 mV-1.5 V). As a result, step (3) is the slowest step in the sequence, limiting the rate of CO removal, thereby allowing poisoning of the electrocatalyst to occur. This applies in particular to a proton exchange membrane fuel cell which is especially sensitive to CO poisoning because of its low operating temperatures.

10 **[0011]** One approach for improving the cathodic performance of an electrocatalyst during the reduction of oxygen and/or the anodic performance during the oxidation of hydrogen or methanol is to employ an electrocatalyst which is more active, corrosion resistant, and/or more poison tolerant. For example, increased tolerance to CO has been reported by alloying platinum and
15 ruthenium at a 50:50 atomic ratio (see, D. Chu and S. Gillman, J. Electrochem. Soc. 1996, 143, 1685). The electrocatalysts proposed to-date, however, leave room for further improvement.

BRIEF SUMMARY OF THE INVENTION

20 **[0012]** Briefly, therefore, the present invention is directed to a composition for use as a catalyst in oxidation or reduction reactions, in for example fuel cells, the composition comprising platinum and copper, wherein (i) the concentration of platinum is greater than 50 atomic percent and less than about 80 atomic percent, and (ii) the composition has a particle size which is less than 35 angstroms (Å).

25 **[0013]** The present invention is further directed to the preceding composition wherein the sum of the concentrations of platinum and copper therein is greater than about 95 atomic percent.

30 **[0014]** The present invention is still further directed to one of the preceding compositions wherein said composition comprises an alloy of the recited metals, or alternatively consists essentially of an alloy of the recited metals.

35 **[0015]** The present invention is still further directed to a supported electrocatalyst powder for use in electrochemical reactor devices, the supported electrocatalyst powder comprising any of the foregoing catalyst compositions on electrically conductive support particles.

[0016] The present invention is also directed to a fuel cell electrode, the fuel cell electrode comprising electrocatalyst particles and an electrode substrate upon which the electrocatalyst particles are deposited, the electrocatalyst particles comprising any of the foregoing catalyst compositions.

5 [0017] The present invention is also directed to a fuel cell comprising an anode, a cathode, a proton exchange membrane between the anode and the cathode, and any of the foregoing catalyst compositions, for the catalytic oxidation of a hydrogen-containing fuel or the catalytic reduction of oxygen.

[0018] The present invention is further directed to a method for the
10 electrochemical conversion of a hydrogen-containing fuel and oxygen to reaction products and electricity in the foregoing fuel cell, said fuel cell further comprising an electrically conductive external circuit connecting the anode and cathode. The method comprises contacting the hydrogen-containing fuel or the oxygen and the catalyst composition to catalytically oxidize the hydrogen-containing fuel
15 or catalytically reduce the oxygen.

[0019] The present invention is still further directed to a fuel cell electrolyte membrane, and/or fuel cell electrode, having deposited on a surface thereof a layer of an unsupported catalyst composition, said unsupported catalyst composition layer comprising any of the foregoing catalyst
20 compositions.

[0020] The present invention is still further directed to a method for preparing one of the foregoing catalyst compositions from a catalyst precursor composition, said precursor composition comprising platinum and copper, wherein the concentration of platinum therein is greater than about 20 atomic
25 percent and less than about 40 atomic percent. The method comprises subjecting said precursor composition to conditions sufficient to remove a portion of the copper present therein, such that the resulting catalyst composition comprises platinum and copper, and wherein the concentration of platinum is greater than 50 atomic percent and less than about 80 atomic
30 percent. Optionally, the catalyst composition may have a particle size which is less than 35 angstroms (Å).

[0021] The present invention is further directed to such a method wherein the catalyst precursor composition is contacted with an acidic solution to solubilize a portion of the copper present therein. Alternatively, the present
35 invention is further directed to such a method wherein the catalyst precursor composition is subjected to an electrochemical reaction, wherein for example a hydrogen-containing fuel and oxygen are converted to reaction products and electricity in a fuel cell comprising an anode, a cathode, a proton exchange

membrane therebetween, the catalyst precursor composition, and an electrically conductive external circuit connecting the anode and cathode. By contacting the hydrogen-containing fuel or the oxygen and the catalyst precursor composition, the hydrogen-containing fuel is oxidized and/or the oxygen is catalytically
5 reduced. As part of this reaction, copper is dissolved *in situ* from the catalyst precursor composition.

[0022] The present invention is still further directed to a method for preparing a catalyst composition from a catalyst precursor composition, said precursor composition comprising platinum and copper, wherein the
10 concentration of platinum therein is less than 50 atomic percent. The method comprises contacting said precursor composition with an acidic solution having a pH which is greater than 0 and less than 7, to solubilize a portion of the copper present therein, such that the resulting catalyst composition comprises platinum and copper, the concentration of platinum therein being greater than 50 atomic
15 percent. Optionally, the platinum concentration of the catalyst precursor may be greater than about 20 atomic percent and less than about 40 atomic percent, and/or the concentration of platinum in the catalyst composition may be greater than 50 atomic percent and less than about 80 atomic percent. Additionally, the catalyst composition may optionally have a particle size which is less than 35
20 angstroms (Å).

[0023] The present invention is still further directed to a method for preparing a catalyst composition from a catalyst precursor composition, said precursor composition comprising platinum and copper, wherein the concentration of platinum therein is less than 50 atomic percent. The method
25 comprises contacting said precursor composition with a solution in air, or alternatively in an atmosphere having a oxygen concentration which is greater than in air, to solubilize a portion of the copper present therein, such that the resulting catalyst composition comprises platinum and copper, the concentration of platinum therein being greater than 50 atomic percent. Optionally, the
30 platinum concentration of the catalyst precursor may be greater than about 20 atomic percent and less than about 40 atomic percent, and/or the concentration of platinum in the catalyst composition may be greater than 50 atomic percent and less than about 80 atomic percent. Additionally, the catalyst composition may optionally have a particle size which is less than 35 angstroms (Å).

35 [0024] The present invention is still further directed to a method of preparing a catalyst composition comprising, or consisting essentially of, an alloy of platinum and copper. The method comprises depositing a copper-containing compound, and optionally a platinum-containing compound, on electrically

conductive support particles, and heating the copper and platinum on said support particles in a reducing atmosphere at a temperature which is greater than about 450°C and less than 800°C for a duration sufficient to form an alloy of copper and platinum, wherein the concentration of platinum in the catalyst composition is greater than about 50 atomic percent and less than about 80 atomic percent. Optionally, the copper and platinum alloy of the catalyst composition has a particle size which is less than 35 angstroms (Å).

[0025] The present invention is still further directed to a method of preparing a catalyst composition comprising an alloy of platinum and copper on electrically conductive support particles. The method comprises: (a) forming a catalyst composition precursor having a platinum concentration that is greater than about 20 atomic percent and less than about 40 atomic percent, by (i) depositing a copper-containing compound on electrically conductive support particles, (ii) depositing a platinum-containing compound on electrically conductive support particles, and (iii) heating said deposited compounds on said support particles in a reducing atmosphere at a temperature which is greater than about 450°C for a duration of at least 2 hours to form an alloy of copper and platinum; and, (b) contacting said precursor composition with an acidic solution in air, or alternatively in an atmosphere having an oxygen concentration which is greater than in air, to solubilize a portion of the copper present therein.

[0026] The present invention is further directed to one of the foregoing methods for preparing the catalyst composition wherein the sum of the concentrations of platinum and copper in the catalyst composition precursor, and/or the catalyst composition, is greater than about 95 atomic percent.

[0027] It is to be understood that the present invention encompasses all of the various potential combinations of limitations, recited above and/or elsewhere herein, which relate to the catalyst composition, the catalyst composition precursor, and/or the methods of preparing the catalyst composition, without departing from the intended scope of the present invention.

[0028] The foregoing, as well as other features and advantages of the present invention, will become more apparent from the following description and accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] Figure 1 is a photograph of a TEM image of a carbon support with catalyst nanoparticles deposited thereon, in accordance with the present invention.

5 [0030] Figure 2 is an exploded, schematic structural view showing members of a fuel cell.

[0031] Figure 3 is cross-sectional view of the assembled fuel cell of Figure 2.

10 [0032] Figure 4 is a photograph of an electrode array comprising thin film catalyst compositions deposited on individually addressable electrodes, in accordance with the present invention.

[0033] Figure 5 is a X-ray diffraction plot of a supported platinum-copper alloy powder comprising carbon supports with platinum-copper alloy nanoparticles deposited on the carbon supports, such as that illustrated in
15 Figure 1.

[0034] It is to be noted that corresponding reference characters indicate corresponding parts throughout the drawings.

DETAILED DESCRIPTION OF THE INVENTION

20 [0035] The present invention is directed to a composition having catalytic activity for use in, for example, oxidation and/or reduction reactions of interest in a polyelectrolyte membrane fuel cell (e.g., an electrocatalyst), the composition comprising, as further detailed herein, platinum and copper.

[0036] In this regard it is to be noted that, in general, it is desirable, but
25 not essential, to reduce the cost of a catalyst composition to be used in such reactions, particularly when used in a fuel cell. One approach for reducing the cost of the catalyst composition is to decrease the amount of noble metals (such as platinum) used to produce it. Typically, however, as the concentrations of noble metals are decreased, catalyst compositions tend to become more
30 susceptible to corrosion and/or the absolute activity may be diminished. Thus, it is typically desirable to achieve the most activity per weight percent of noble metals (see, e.g., End Current Density /Weight Fraction of Pt, as set forth in Tables A-O, infra). Preferably, this is accomplished without compromising, for example, the life cycle of the fuel cell in which the catalyst composition is placed.
35 In addition to, or as an alternative to, reducing cost by limiting the noble metal concentration, a catalyst composition of the present invention may be selected

because it represents an improvement in corrosion resistance and/or activity compared to platinum (e.g., at least a 3 times increase in electrocatalytic activity compared to platinum).

[0037] The present invention is thus directed to a composition that has
5 catalytic activity in oxidation and/or reduction reactions, and that comprises platinum and copper. Optionally, the catalyst composition of the present invention may be in the form of an alloy of these metals, the composition for example consisting essentially of an alloy containing these metals. Alternatively, the catalyst composition of the present invention may comprise these metals, a
10 portion of which is in the form of an alloy, the composition for example having alloy particles intermixed with oxide particles as a coating, as a pseudo-support, and/or a simple mixture.

[0038] The catalyst composition of the present invention comprises amounts of platinum and copper which are sufficient for these metals to play a
15 role in the catalytic activity and/or crystallographic structure of the catalyst composition. Stated another way, the concentrations of platinum and copper in the present catalyst composition are such that the presence of the metals would not be considered an impurity. For example, the concentrations of each of platinum and copper are at least about 0.1, 0.5, 1, or even 2 atomic percent,
20 wherein the sum of the concentrations of platinum and copper may be, for example, greater than about 95 atomic percent, about 96 atomic percent, about 97 atomic percent, about 98 atomic percent, or even about 99 atomic percent. Advantageously and surprisingly, it has been discovered that catalyst compositions comprising platinum and copper (e.g., alloys) may exhibit
25 favorable electrocatalytic activity while having reduced amounts of platinum, as compared to, for example, a platinum standard.

[0039] In this regard it is to be noted that the catalyst compositions of the present invention may optionally consist essentially of the platinum and copper (e.g., impurities that play little, if any, role in the catalytic activity and/or
30 crystallographic structure of the catalyst may be present to some degree), the concentrations of the metals being within any one or more of the ranges set forth herein for an individual metal, or for the combination of metals. Stated another way, the concentration of a metallic or non-metallic element other than platinum and copper may optionally not exceed what would be considered an impurity
35 (e.g., less than 1, 0.5, 0.1, or 0.01 atomic percent). However, it is possible that the catalyst of the present invention may alternatively comprise platinum and copper, as well as other constituents, including for example platinum and/or copper oxides and/or carbides. It is therefore to be noted that in some

embodiments the total concentration of platinum and copper may be less than about 100 percent of the metal atoms present therein.

[0040] It is to be further noted that in one or more embodiments of the present invention, platinum and/or copper are substantially in their metallic oxidation states. Stated another way, the average oxidation state of platinum and/or copper are at or near zero. Although in such embodiments there may be portions of the catalyst composition wherein the oxidation states of one or both of platinum and/or copper are greater than zero, the average oxidation states of these elements throughout the entire composition is less than the lowest commonly occurring oxidation state for that particular element (e.g., the lowest commonly occurring oxidation states for platinum and copper are 2 and 1, respectively). Therefore, the average oxidation states of platinum may be, in order of increasing preference, less than 2, 1.5, 1, 0.5, 0.1, or 0.01, or even zero, while the average oxidation state of copper may be, in order of increasing preference, less than 1, 0.5, 0.1, or 0.01, or even zero.

[0041] It is to be still further noted, however, that in an alternative embodiment of the present invention, the platinum and/or copper may not be substantially present in their metallic oxidation states. Stated another way, in one or more embodiments of the present invention, the platinum and/or copper present in the catalyst composition may have an average oxidation state that is greater than zero (the platinum and/or copper being present in the catalyst, for example, as an oxide or as a carbide).

1. *Catalyst Compositions*

A. *Constituent Concentrations*

[0042] The concentration of platinum in the catalyst composition of the present invention is greater than about 50 atomic percent, and typically is less than about 80 atomic percent (e.g., greater than about 55, about 60 or even about 65 atomic percent, and less than about 80, about 75, or even about 70 atomic percent). Accordingly, the platinum concentration may, for example, be in the range of from about 60 atomic percent to about 80 atomic percent, or preferably in the range of from about 65 to about 75 atomic percent.

[0043] In this regard it is to be noted, however, that the scope of the present invention is intended to encompass all of the various platinum concentration range permutations possible herein, in view of the above-noted maxima and minima.

[0044] The concentration of copper in the catalyst composition of the present invention is less than about 50 atomic percent, and typically is greater than about 20 atomic percent (e.g., less than about 45, about 40 or even about 35 atomic percent, and greater than about 20, about 25, or even about 30 atomic percent). Accordingly, the copper concentration may, for example, be in the range of from about 20 atomic percent to about 40 atomic percent, or preferably in the range of from about 25 to about 35 atomic percent.

[0045] In this regard it is to be noted, however, that the scope of the present invention is intended to encompass all of the various copper concentration range permutations possible herein, in view of the above-noted maxima and minima.

[0046] It is to be further noted that the catalyst composition of the present invention may encompass any of the various combinations of platinum and copper concentrations and/or ranges of concentrations set forth above without departing from its intended scope. For example, the catalyst composition of the present invention may comprises platinum and copper, wherein: (i) the sum of the concentrations of platinum and copper is greater than about 95 atomic percent, about 96 atomic percent, about 97 atomic percent, about 98 atomic percent, or even about 99 atomic percent; and (ii) the concentration of platinum is greater than 50 atomic percent and less than about 80 atomic percent, or greater than about 60 atomic percent and less than about 80 atomic percent, greater than about 55 atomic percent and less than about 75 atomic percent.

B. Particle Size

[0047] It is to be noted that, as additionally detailed elsewhere herein, one or more of the methods (e.g., freeze-drying, alloying, washing) and/or conditions thereof (e.g., alloying temperature and/or duration, pH of the acidic solution and/or the atmosphere employed when dissolving, for example, copper from the catalyst composition) employed to prepare the catalyst compositions of the present invention may be controlled in order to control or limit the particle size of the resulting catalyst composition. Preferably, one or more of these methods and/or method conditions are controlled such that the catalyst composition has an average particle size, on for example the electrically conductive support, which is no greater than about 5 nm (50 Å), more preferably no greater than about 4 nm (40 Å), still more preferably no greater than about 3.5 nm (35 Å), still more preferably no greater than about 3 nm (30 Å), still more

preferably no greater than about 2.5 nm (25 Å), still more preferably no greater than about 2 nm (20 Å), still more preferably no greater than about 1.5 nm (15 Å), and still more preferably no greater than about 1 nm (10 Å); the average size of the catalyst composition may therefore be in the range of, for example, 5 greater than about 10 Å to less than 50 Å, greater than about 15 Å to less than 40 Å, greater than about 20 Å to less than 35 Å, greater than about 20 Å to less than 30 Å, or greater than about 25 Å to less than 30 Å.

[0048] It is to be noted that, optionally, the size distribution of the catalyst composition particles is such that at least about 75 percent, preferably 80 10 percent, more preferably 85 percent, and still more preferably 90 percent or more of the particles are within about 75 to about 125 percent, and preferably within about 90 to about 110 percent of the average particle size. Additionally, or alternatively, it is to be further noted that the catalyst composition may have a lattice parameter of less than 3.729 Å (e.g., less than 3.725, 3.720, 3.715, 3.710, 15 3.705, 3.700, 3.695, 3.690, 3.685, etc.), ranging from example from 3.725 to about 3.685, or from about 3.720 to about 3.690, or from about 3.715 to about 3.695.

C. *Compositional Drift*

[0049] As has been reported elsewhere, subjecting a catalyst 20 composition to an electrocatalytic reaction (e.g., the operation of a fuel cell) may change the composition by leaching one or more constituents (e.g., copper) from the catalyst (see, e.g., Catalysis for Low Temperature Fuel Cells Part 1: The Cathode Challenges, T.R. Ralph and M.P. Hogarth, Platinum Metals Rev., 2002, 46, (1), p. 3-14). Without being held to any particular theory, it is believed 25 that this leaching effect may potentially act to increase the activity of the catalyst by increasing the surface area and/or by changing the surface composition of the catalyst. In fact, the purposeful leaching of catalyst compositions after synthesis to increase the surface area has been disclosed by Itoh et al. (see, e.g., U.S. Pat. No. 5,876,867). Accordingly, it is to be noted that the 30 concentrations, concentration ranges, and atomic ratios detailed herein for the catalyst compositions of the present invention are intended to include the bulk stoichiometries, any surface stoichiometries resulting therefrom, and modifications of the bulk and/or surface stoichiometries that result by subjecting the catalyst compositions of the present invention to a reaction (e.g., an 35 electrocatalytic reaction) of interest.

2. *Catalyst Composition Precursors*

A. *Washing/Leaching*

[0050] With respect to the above-noted compositional drift that has been observed in use, it is to be further noted that, as illustrated by the results presented in, for example, Tables R1 and R2 herein (see Example 5), it has further been observed that the performance (e.g., activity) of a catalyst composition of the present invention, having a platinum concentration which is greater than 50 atomic percent in use (i.e., after drift has occurred), is improved as compared to a composition that has been prepared to have a concentration of 50 atomic percent platinum or greater prior to use. Stated another way, it has been observed that a catalyst composition comprising platinum and copper as detailed herein which, after the loss of for example copper therefrom, has a platinum concentration that is greater than 50 atomic percent performs better than a catalyst composition that has been prepared to initially have the same, or similar, composition (compare, for example, the relative activities reported for: (i) samples HFC 655, having an initial target composition of $\text{Pt}_{25}\text{Cu}_{75}$ and a final composition of $\text{Pt}_{52}\text{Cu}_{48}$ v. HFC 657, having a comparable composition of $\text{Pt}_{50}\text{Cu}_{50}$).

[0051] Accordingly, the present invention is further directed to a precursor to the catalyst compositions of the present invention, the precursor comprising platinum and copper, wherein the concentration of platinum therein is less than 50 atomic percent, and preferably is about 45 atomic percent, more preferably about 40 atomic percent, still more preferably about 35 atomic percent, still more preferably about 30 atomic percent, still more preferably about 25 atomic percent, and still more preferably about 20 atomic percent (preferably ranging, for example, from greater than about 20 to about 40 atomic percent, or more preferably from about 25 to about 35 atomic percent). Additionally, the sum of platinum and copper in the catalyst composition precursor may optionally be at least about 95 atomic percent, preferably about 96 atomic percent, more preferably about 97 atomic percent, still more preferably about 98 atomic percent, and still more preferably about 99 atomic percent or more. The concentration of copper in the precursor may therefore be greater than 50 atomic percent (e.g., about 55 atomic percent, 60 atomic percent, 65 atomic percent, 70 atomic percent, 75 atomic percent, or 80 atomic percent), the concentration ranging, for example, from about 60 to about 80 atomic percent, or from about 65 to about 75 atomic percent.

[0052] The present invention is therefore additionally directed to a method for the preparation of a catalyst composition as set forth herein from a catalyst precursor composition, said precursor composition comprising platinum and copper as set forth herein above (e.g., the sum of the concentrations of platinum and copper therein being, for example, greater than about 95 atomic percent, and the concentration of platinum therein being less than 50, 45, 40, etc. atomic percent). Generally speaking, the method comprises subjecting said precursor composition to conditions sufficient to remove a portion of the copper present therein (such that a catalyst composition, as set forth elsewhere herein is obtained, the catalyst composition comprising, for example, platinum and copper wherein the sum of the concentrations thereof is greater than about 95 atomic percent and the concentration of platinum therein is greater than 50, 55, 60, etc. atomic percent). Optionally, the method, and/or method conditions, are selected in order to obtain a catalyst composition having a particle size that is less than 35 Å (e.g., greater than 20 Å to less than 35 Å, or greater than about 25 Å to less than 30 Å).

[0053] In one preferred embodiment of the above-noted method, the catalyst precursor composition is contacted with an acidic solution to wash or remove a portion of the copper present therein out of the precursor. For example, a given weight of the catalyst precursor composition is contacted with a quantity of a perchloric acid (HClO_4) solution (e.g., 1 M, having a pH of about 0), heated (e.g., about 90 to about 95°C) for a period of time (e.g., about 60 minutes), filtered, and then repeatedly washed with water. The resulting filtrate typically has a pale blue color, indicating the presence of copper ions. The precursor composition is preferably washed a second time, the solid cake isolated from the first filtration step being collected and then subjected to substantially the same sequence of steps as previously performed, the cake being agitated sufficiently to break it apart prior to and/or during the time spent heating the cake/acid solution mixture back up to the desired temperature. After the final filtration has been performed, the isolated cake is dried (e.g., heated at about 90°C for about 48 hours).

[0054] It is to be noted that, in one approach to the above-noted method, the acidic solution may have a pH which is greater than 0 and less than 7, and preferably has a pH which is greater than about 0.25 and less than about 5, still more preferably has a pH which is greater than about 0.5 and less than about 3, and still more preferably has a pH which is greater than about 0.75 and less than about 1.5. Additionally and/or alternatively, the above-noted method is

carried out in the presence of in air, or alternatively in an atmosphere having an oxygen concentration which is greater than in air.

[0055] It is to be further noted, however, that in an alternative embodiment the catalyst precursor composition may be exposed to conditions
5 common within a fuel cell (e.g., immersion in an electrochemical cell containing an aqueous 0.5 M H_2SO_4 electrolyte solution maintained at room temperature, such as described in Example 4, herein below), in order to leach copper from the precursor. Alternatively, the precursor may be directly subjected to an electrochemical reaction wherein, for example, a hydrogen-containing fuel and
10 oxygen are converted to reaction products and electricity in a fuel cell comprising an anode, a cathode, a proton exchange membrane therebetween, the catalyst precursor composition, and an electrically conductive external circuit connecting the anode and cathode. By contacting the hydrogen-containing fuel or the oxygen and the catalyst precursor composition, the hydrogen-containing
15 fuel is oxidized and/or the oxygen is catalytically reduced. As part of this reaction, copper is thus dissolved *in situ* from the catalyst precursor composition. After this reaction has been allowed to continue for a length of time sufficient to obtain a substantially stable composition (i.e., a composition wherein the concentration of platinum and/or copper remain substantially
20 constant), the composition may be removed from the cell and used as a catalyst composition in an future fuel cell reaction of interest.

[0056] It is to be still further noted that the method of removing a portion of, for example, the copper from the catalyst composition precursor may be other than herein described without departing from the scope of the present
25 invention. For example, alternative solutions may be used (e.g., $\text{HCF}_3\text{SO}_3\text{H}$, NAFIONTM, HNO_3 , HCl , H_2SO_4 , $\text{CH}_3\text{CO}_2\text{H}$), and/or alternative concentrations (e.g., about 0.05 M, 0.1 M, 0.5 M, 1 M, 2 M, 3 M, 4 M, 5 M, etc.), and/or alternative temperatures (e.g., about 25°C, 35°C, 45°C, 55°C, 65°C, 75°C, 85°C, etc.), and/or alternative washing times or durations (e.g., about 5 minutes, 10
30 minutes, 20 minutes, 30 minutes, 40 minutes, 50 minutes, 60 minutes or more), and/or alternative numbers of washing cycles (e.g., 1, 2, 3, 4, 5 or more), and/or alternative washing techniques (e.g., centrifugation, sonication, soaking, electrochemical techniques, or a combination thereof), and/or alternative washing atmospheres (e.g., ambient, oxygen-enriched, argon), as well as
35 various combinations thereof (selected using means common in the art).

[0057] It is to be still further noted that the compositions of the precursors recited above, and/or elsewhere herein, refer to the overall stoichiometries, or bulk stoichiometries, of a prepared precursor composition,

before being subjected to washing or *in situ* leaching conditions of some kind (e.g., subjected to use conditions in an electrocatalytic cell). Accordingly, a reported precursor composition (e.g., a precursor composition comprising or consisting essentially of an alloy of the recited metals) is an average

5 stoichiometry over the entire volume of the prepared precursor composition, and therefore, localized stoichiometric variations may exist. For example, the volume of a particle precursor composition comprising the surface and the first few atomic layers inward therefrom may differ from the bulk stoichiometry. Likewise, within the bulk of the particle there may be stoichiometric variations.

10 The surface stoichiometry corresponding to a particular bulk stoichiometry is highly dependant upon the method and conditions under which the precursor composition is prepared. As such, precursor compositions having the same bulk stoichiometry may have significantly different surface stoichiometries. Without being bound to a particular theory, it is believed the differing surface

15 stoichiometries are due at least in part to differences in the atomic arrangements, chemical phases and homogeneity of the compositions.

B. Precursor Lattice Parameters

[0058] The above-noted catalyst composition precursor may also be characterized by its lattice parameter. Specifically, a change in a lattice

20 parameter may be indicative of a resulting change in the size of the respective metal constituents. For example, the 12-coordinate metallic radii of platinum and copper are 1.387 Å and 1.278 Å, respectively. As one metal is substituted for another, the average metal radius and, consequently, the observed lattice parameter may be expected to shrink or expand accordingly. Thus, the average

25 radius may be used as an indicator of lattice changes as a function of stoichiometry, or alternatively, as an indicator of stoichiometry based on observed lattice parameters. It should be noted, however, that while average radii may be useful as a general rule, actual measurements should be expected to conform only in a general manner because local ordering, significant size

30 disparity between atoms, significant changes in symmetry, and/or other factors may produce values that are inconsistent with expectations. Occasionally, the use of alternative metallic radii may be useful. One such alternative radius concept approximates metal radii using known crystallographically ordered Pt-based alloys such as PtCu (cubic symmetry is maintained) instead of pure

35 metals. In this case, the same close-packed geometric arguments are relevant with the exception that the lattice parameter of the ordered metal alloy is used in

conjunction with the accepted 12-coordinate metallic radius of platinum. According to the alternative radius concept, it is believed that the effective radius of copper is about 1.284 Å.

[0059] In one embodiment of the present invention, the catalyst
5 composition precursor comprises, or consists essentially of, an platinum-copper alloy having a lattice parameter of no more than 3.777 Å, which is believed to generally correspond to an alloy comprising at least 50 atomic percent copper. In another embodiment, the catalyst composition precursor alloy has a lattice
10 parameter of between about 3.674 and about 3.765 Å, which is believed to generally correspond to an alloy comprising between about 15 and about 45 atomic percent platinum and between about 55 and about 85 atomic percent copper. In yet another embodiment, the catalyst composition precursor alloy has a lattice parameter of about 3.689 and about 3.750 Å, which is believed to generally correspond to an alloy comprising between about 20 and about 40
15 atomic percent platinum and between about 60 and about 80 atomic percent copper. In still another embodiment, the catalyst composition precursor alloy has a lattice parameter of between about 3.704 and about 3.745 Å, which is believed to generally correspond to an alloy comprising between about 25 and about 35 atomic percent platinum and between about 65 and about 75 atomic
20 percent copper.

[0060] In this regard it is to be noted that the lattice parameters recited above are for the precursor catalyst compositions (i.e., compositions prior to washing or leaching to remove a portion of, for example, copper therein). It is to be further noted that after washing or leaching, some type of skeleton structure
25 or formation may result in lattice parameters that deviate from the above-described ranges versus compositions.

3. *Formation of Catalyst Composition Precursors Comprising/Consisting Essentially of an Alloy*

[0061] The catalyst composition, and/or the catalyst composition
30 precursor, of the present invention may consist essentially of an alloy of platinum and copper. Alternatively, the catalyst composition, and/or the catalyst composition precursor, of the present invention may comprise an alloy of platinum and copper; that is, one or both of these may alternatively comprise an alloy of these metals, and optionally one or more of these metals in a non-alloy
35 form (e.g., a platinum and/or copper salt and/or oxide and/or carbide).

[0062] Such alloys may be formed by a variety of methods. For example, the appropriate amounts of the constituents (e.g., metals) may be mixed together and heated to a temperature above the respective melting points to form a molten solution of the metals that is cooled and allowed to solidify.

5 **[0063]** Typically, the catalyst compositions of the present invention, and/or the precursors thereto, are used in a powder form to increase the surface area, which in turn increases the number of reactive sites, and thus leads to improved efficiency of the cell in which the catalyst compositions are being used. Thus, a formed catalyst composition alloy, and/or the precursor thereto, may be
10 transformed into a powder after being solidified (e.g., by grinding), or during solidification (e.g., spraying molten alloy and allowing the droplets to solidify). In this regard it is to be noted, however, that in some instances it may be advantageous to evaluate alloys for electrocatalytic activity in a non-powder form, as further described and illustrated elsewhere herein (see, e.g., Examples
15 1 and 2, *infra*).

[0064] To further increase surface area and efficiency, a catalyst composition alloy (i.e., a catalyst composition comprising or consisting essentially of an alloy), and/or the precursor thereto, may be deposited over the surface of electrically conductive supports (e.g., carbon black) for use in a fuel
20 cell. One method for loading a catalyst composition or precursor alloy onto supports typically comprises depositing metal-containing (e.g., platinum and/or copper) compounds onto the supports, converting these compounds to metallic form, and then alloying the metals using a heat-treatment in a reducing atmosphere (e.g., an atmosphere comprising an inert gas such as argon and/or
25 a reducing gas such as hydrogen). One method for depositing these compounds involves the chemical precipitation thereof onto the supports. The chemical precipitation method is typically accomplished by mixing supports and sources of the metal compounds (e.g., an aqueous solution comprising one or more inorganic metal salts) at a concentration sufficient to obtain the desired
30 loading of the catalyst composition, or precursor thereto, on the supports, after which precipitation of the compounds is initiated (e.g., by adding an ammonium hydroxide solution). The slurry is then typically filtered from the liquid under vacuum, washed with deionized water, and dried to yield a powder that comprises the metal compounds on the supports.

35 **[0065]** Another method for depositing the metal compounds comprises forming a suspension comprising a solution and supports suspended therein, wherein the solution comprises a solvent portion and a solute portion that comprises the metal compound(s) being deposited. The suspension is frozen to

deposit (e.g., precipitate) the compound(s) on the support particles. The frozen suspension is then freeze-dried to remove the solvent portion, leaving a freeze-dried powder comprising the supports and the deposits of the metal compound(s) on the supports.

5 **[0066]** Since the method may involve sublimation of the solvent portion from the frozen suspension, the solvent portion of the solution in which the supports are suspended preferably has an appreciable vapor pressure below its freezing point. Examples of such sublimable solvents that also dissolve many metal-containing compounds and metals include water, alcohols (e.g., methanol,
10 ethanol, etc.), acetic acid, carbon tetrachloride, ammonia, 1,2-dichloroethane, N,N-dimethylformamide, formamide, etc.

[0067] The solution in which the supports are dispersed/suspended provides the means for delivering the metal species which is to be deposited onto the surfaces of the supports. The metal species may be the final desired
15 form, but in many instances it is not. If the metal species is not a final desired form, the deposited metal species may be subsequently converted to the final desired form. Examples of such metal species that may be subsequently converted include inorganic and organic metal compounds such as metal halides, sulfates, carbonates, nitrates, nitrites, oxalates, acetates, formates, etc.
20 Conversion to the final desired form may be made by thermal decomposition, chemical reduction, or other reaction. Thermal decomposition, for example, is brought about by heating the deposited metal species to obtain a different solid material and a gaseous material. In general, as is known, thermal decomposition of halides, sulfates, carbonates, nitrates, nitrites, oxalates,
25 acetates, and formates may be carried out at temperatures between about 200 and about 1,200°C.

[0068] If conversion of the deposited metal species to the final desired form is to occur, the deposited metal species is usually selected such that any unwanted by-products from the conversion can be removed from the final
30 product. For example, during thermal decomposition the unwanted decomposition products are typically volatilized. To yield a final product that is a metal alloy, the deposited metal species are typically selected so that the powder comprising the deposited metal species may be reduced without significantly altering the uniformity of the metal deposits on the surface of the
35 supports and/or without significantly altering the particle size of the final powder (e.g., through agglomeration).

[0069] Nearly any metal may be deposited onto supports by one or more of the methods noted herein, provided that the metal or compound containing the metal is capable of being dissolved in a suitable medium (i.e., a solvent). Likewise, nearly any metal may be combined with, or alloyed with, any other metal provided the metals or metal-containing compounds are soluble in a suitable medium.

[0070] The solute portion may comprise an organometallic compound and/or an inorganic metal-containing compound as a source of the metal species being deposited. In general, organometallic compounds are more costly, may contain more impurities than inorganic metal-containing compounds, and may require organic solvents. Organic solvents are more costly than water and typically require procedures and/or treatments to control purity or negate toxicity. As such, organometallic compounds and organic solvents are generally not preferred. An example of an appropriate inorganic salt is $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, which is highly soluble in water. As a result, water is often considered to be a preferred solvent. In some instances, it is desirable for an inorganic metal-containing compound to be dissolved in an acidic solution prior to being mixed with other inorganic metal-containing compounds.

[0071] To form a catalyst alloy, or catalyst precursor alloy, having a particular composition or stoichiometry, the amounts of the various metal-containing source compounds necessary to achieve that composition are determined in view thereof. If the supports have a pre-deposited metal, the loading of the pre-deposited metal on the supports is typically taken into account when calculating the necessary amounts of metal-containing source compounds. After the appropriate amounts of the metal-containing compounds are determined, the solution may be prepared by any appropriate method. For example, if all the selected metal-containing source compounds are soluble at the desired concentration in the same solvent at room temperature, they may merely be mixed with the solvent. Alternatively, the suspending solution may be formed by mixing source solutions, wherein a source solution comprises a particular metal-containing source compound at a particular concentration. If, however, all of the selected compounds are not soluble at the same temperature when mixed together (either as powders in a solvent or as source solutions), the temperature of the mixture may be increased to increase the solubility limit of one or more of the source compounds so that the suspending solution may be formed. In addition to adjusting solubility with temperature, the stability of the suspending solution may be adjusted, for example, by the addition of a buffer, by the addition of a complexing agent, and/or by adjusting the pH.

[0072] In addition to varying the amounts of the various metals to form alloys having different compositions, this method allows for a wide variation in the loading of the metal onto the supports. This is beneficial because it allows for the activity of a supported catalyst composition (e.g., an electrocatalyst powder) to be maximized. The loading may be controlled in part by adjusting the total concentration of the various metals in the solution while maintaining the relative amounts of the various metals. In fact, the concentrations of the inorganic metal-containing compounds may approach the solubility limit for the solution. Typically, however, the total concentration of inorganic metal-containing compounds in the solution is between about 0.01 M and about 5 M, which is well below the solubility limit. In one embodiment, the total concentration of inorganic metal-containing compounds in the solution is between about 0.1 M and about 1 M. Concentrations below the solubility limit are used because it is desirable to maximize the loading of the supported catalysts without decreasing the surface area of the metal deposits. Depending, for example, on the particular composition, the size of the deposits, and the uniformity of the distribution of deposits on the supports, the loading may typically be between about 5 and about 60 weight percent. In one embodiment, the loading is between about 15 and about 45 or about 55 weight percent, or between about 20 and about 40 or about 50 weight percent. In another embodiment, the loading is about 20 weight percent, about 40 weight percent, or about 50 weight percent.

[0073] The supports upon which the metal species (e.g., metal-containing compound) is to be deposited may be of any size and composition that is capable of being dispersed/suspended in the solution during the removal of heat to precipitate the metal species thereon. The maximum size depends on several parameters including agitation of the suspension, density of the supports, specific gravity of the solution, and the rate at which heat is removed from the system. In general, the supports are electrically conductive and are useful for supporting catalytic compounds in fuel cells. Such electrically conductive supports are typically inorganic, for example, carbon supports. However, the electrically conductive supports may comprise an organic material such as an electrically conductive polymer (see, e.g., in U.S. Pat. No. 6,730,350). Carbon supports may be predominantly amorphous or graphitic and they may be prepared commercially, or specifically treated to increase their graphitic nature (e.g., heat treated at a high temperature in vacuum or in an inert gas atmosphere) thereby increasing corrosion resistance. Carbon black support particles may have a Brunauer, Emmett and Teller (BET) surface area up to

about 2000 m²/g. It has been reported that satisfactory results are achieved using carbon black support particles having a high mesoporous area, e.g., greater than about 75 m²/g (see, e.g., Catalysis for Low Temperature Fuel Cells Part 1: The Cathode Challenges, T.R. Ralph and M.P. Hogarth, Platinum Metals Rev., 2002, 46, (1), p. 3-14). Experimental results to-date indicate that a surface area of about 500 m²/g is preferred.

[0074] In another embodiment, the supports may have a pre-deposited material thereon. For example, when the final composition of the deposits on the carbon supports is a platinum alloy, it may be advantageous to use a carbon supported platinum powder. Such powders are commercially available from companies such as Johnson Matthey, Inc., of New Jersey and E-Tek Div. of De-Nora, N.A., Inc., of Somerset, New Jersey and may be selected to have a particular loading of platinum. The amount of platinum loading is selected in order to achieve the desired stoichiometry of the supported metal alloy. Typically, the loading of platinum is between about 5 and about 60 weight percent. Preferably, the loading of platinum is between about 15 and 45 weight percent. The size (i.e., the maximum cross-sectional length) of the platinum deposits is typically less than about 20 nm. For example, the size of the platinum deposits may be less than about 10 nm, 5 nm, 2 nm, or smaller; alternatively, the size of the platinum deposits may be between about 2 and about 3 nm. Experimental results to-date indicate that a desirable supported platinum powder may be further characterized by having a platinum surface area of between about 150 and about 170 m²/g (determined by CO adsorption), a combined carbon and platinum surface area of between about 350 and about 400 m²/g (determined by N₂ adsorption), and an average support size that is between about 100 and about 300 nm.

[0075] The solution and supports are mixed according to any appropriate method to form the dispersion/suspension, using means known in the art. Exemplary methods of mixing include magnetic stirring, insertion of a stirring structure or apparatus (e.g., a rotor), shaking, sonication, or a combination of the foregoing methods. Provided that the supports can be adequately mixed with the solution, the relative amounts of supports and solution may vary over a wide range. For example, when preparing carbon supported catalysts using an aqueous suspension comprising dissolved inorganic metal-containing compounds, the carbon supports typically comprise between about 1 and about 30 weight percent of the suspension. Preferably, however, the carbon supports comprise between about 1 and about 15 weight percent of the suspension, between about 1 and about 10 weight percent of the suspension, between about

3 and about 8 weight percent of the suspension, between about 5 and about 7 weight percent of the suspension, or about 6 weight percent of the suspension.

[0076] In this regard it is to be noted that the above-referenced amounts of carbon supports in suspension may apply equally to other, non-carbon supports noted herein, or which are known in the art.

[0077] The relative amounts of supports and solution may also be described in terms of volumetric ratios. For example, the dispersion/suspension may have a volumetric ratio of support particles to solution or solvent that is at least about 1:10. Specifying a minimum volumetric ratio indicates that the volume of support particles may be increased relative to the volume of solution or solvent. As such, the volume ratio of support particles to solution or solvent may more preferably be at least about 1:8, about 1:5, or even about 1:2.

[0078] In one method of preparation, the solution and supports described or illustrated herein are mixed using sonication at a power and for a duration sufficient to form a dispersion/suspension in which the pores of the supports are impregnated with the solution and/or the supports are uniformly distributed throughout the solution. If the dispersion/suspension is not uniformly mixed (i.e., the supports are not uniformly impregnated with the solution and/or the supports are not uniformly distributed throughout the solution), the deposits formed on the supports will typically be non-uniform (e.g., the loading of the metal species may vary among the supports, the size of the deposits may vary significantly on a support and/or among the supports, and/or the composition of the deposits may vary among the supports). Although a uniform mixture, or distribution of supports in the solution, is generally preferred, there may be circumstances in which a non-uniform mixture, or distribution of supports in the solution, is desirable.

[0079] When a freeze-drying method of preparation is employed, typically the uniformity of the distribution of particles in the dispersion/suspension is maintained throughout the removal of heat therefrom. This uniformity may be maintained by continuing the mixing of the dispersion/suspension as it is being cooled. The uniformity may, however, be maintained without mixing by the viscosity of the dispersion/suspension. The actual viscosity needed to uniformly suspend the support particles depends in large part on the amount of support particles in the dispersion/suspension and the size of the support particles. To a lesser degree, the necessary viscosity depends on the density of the support particles and the specific gravity of the solution. In general, the viscosity is typically sufficient to prevent substantial settling of the support particles as the heat is being removed from the

suspension to precipitate the deposits, and/or, if desired, until the dispersion/suspension is solidified by the freezing of the solution or solvent. The degree of settling, if any, may be determined, for example, by examining portions of the solidified or frozen suspension. Typically, substantial settling would be considered to have occurred if the concentration of supports in any two portions varies by more than about $\pm 10\%$. When preparing a carbon supported catalyst powder, or precursors thereto, in accordance with the freeze-drying method, the viscosity of the suspension/dispersion is typically sufficient to prevent substantial settling for at least about 4 minutes. In fact, the viscosity of the suspension/dispersion may be sufficient to prevent substantial settling for at least about 10 minutes, at least about 30 minutes, at least about 1 hour, at least about 6 hours, at least about 12 hours, at least about 18 hours, or even up to about 2 days. Typically, the viscosity of the dispersion/suspension is at least about 5,000 mPa•s.

15 **[0080]** Heat is removed from the dispersion/suspension so that at least a part of the solute portion separates from the solvent portion and deposits (e.g., precipitates) a metal species/precipitated metal onto the supports and/or onto any pre-existing deposits (e.g., a pre-deposited metal and/or pre-deposited metal species formed, for example, by precipitation of incompatible solutes). If the concentration of supports in the suspension is sufficient (e.g., within the ranges set forth above) and enough heat is removed, nearly all of the metal species to be deposited is separated from the solvent portion to form deposits (e.g., precipitates) comprising the metal species on the supports. In one embodiment, the heat is removed to solidify or freeze the dispersion/suspension and form a composite comprising the supports/particulate support with deposits comprising the metal species or a precipitated metal on the supports/particulate support, within a matrix of the solvent portion in a solid state. If the concentration of the solute portion in the solution exceeds the ability of the supports to accommodate deposits of the metal species, some of the solute portion may crystallize within the matrix. If this occurs, such crystals are not considered to be a supported powder.

[0081] In one embodiment of the present invention, the size of the deposits of the metal species is controlled such that the eventually formed deposits of the catalyst composition alloy, or precursor thereto, are as previously noted; that is, the particle size is preferably no greater than about 5 nm (50 Å), more preferably no greater than about 4 nm (40 Å), still more preferably no greater than about 3.5 nm (35 Å), still more preferably no greater than about 3 nm (30 Å), still more preferably no greater than about 2.5 nm (25 Å), still more

preferably no greater than about 2 nm (20 Å), still more preferably no greater than about 1.5 nm (15 Å), and still more preferably no greater than about 1 nm (10 Å); the average size of the catalyst composition may therefore be in the range of, for example, greater than about 10 Å to less than 50 Å, greater than about 15 Å to less than 40 Å, greater than about 20 Å to less than 35 Å, or greater than about 25 Å to less than 30 Å.

[0082] As previously noted, control of the deposit size, or more generally the size of the catalyst composition alloy, or precursor thereto, may be accomplished, at least in part, by maintaining a well-impregnated and uniformly distributed suspension throughout the removal of heat from the system. Additionally, the control of the deposit size may be accomplished by rapidly removing heat from the dispersion/suspension as the compound or compounds are depositing on supports.

[0083] The rapid heat removal may be accomplished by cooling the dispersion/suspension from a temperature of at least about 20°C to a temperature below the freezing point of the solvent at a rate of, for example, at least about 20°C/minute. In order of increasing preference, heat removal may comprise cooling the dispersion/suspension at a rate of at least about 50, 60, 70, 80, 90, or 100°C/minute. As such, the dispersion/suspension may be cooled at a rate that is between about 50 and about 100°C/minute, or at a rate that is between about 60 and about 80°C/minute. Typically, removal of heat is at a rate that allows for the temperature of the suspension to be reduced from a temperature such as room temperature (about 20°C) or higher (e.g., about 100°C) to the freezing point of the solution or solvent within a relatively short period of time (e.g., not more than about 10, 5, or 3 minutes).

[0084] The heat may be removed from the dispersion/suspension by any appropriate method. For example, a container containing a volume of the dispersion/suspension may be placed within a refrigeration unit such as freeze-dryer, a volume of dispersion/suspension may be contacted with a cooled surface (e.g., a plate or container), a volume of dispersion/suspension in a container may be immersed in, or otherwise contacted with, a cryogenic liquid. Advantageously, the same container may also be used during the formation of the dispersion and/or during the separation of solvent from deposited supports. In one embodiment a cover is placed over an opening of the container. Although the cover may completely prevent the escape of any solid matter from the container, the cover preferably allows for a gas to exit the container while substantially preventing the supports from exiting the container. An example of such a cover includes a stretchable film (e.g., PARAFILM) having holes that are,

for example, less than about 500 , 400, or 300 μm in size (maximum length across the hole).

[0085] In one embodiment the dispersion/suspension is cooled at a rate of at least about 20 °C/minute by immersing or contacting a container containing
5 the dispersion/suspension in or with a volume of cryogenic liquid within a cryogenic container sized and shaped so that at least a substantial portion of its surface is contacted with the cryogenic liquid (e.g., at least about 50, 60, 70, 80, or 90 percent of the surface of the dispersion/suspension container). The cryogenic liquid is typically at a temperature that is at least about 20 °C below
10 the freezing point of the solvent. Examples of suitable cryogenic liquids typically include liquid nitrogen, liquid helium, liquid argon, but even less costly media may be utilized (for example, an ice water/hydrous calcium chloride mixture can reach temperatures down to about -55 °C, an acetone/dry ice mixture can reach temperatures down to about -78 °C, and a diethyl ether/dry ice mixture can
15 reach temperatures down to about -100 °C).

[0086] The container may be made of nearly any type of material. Generally, the selected material does not require special handling procedures, can withstand repeated uses without structural failure (e.g., resistant to thermal shock), does not contribute impurities to the suspension (e.g., resistant to
20 chemical attack), and is thermally conductive. For example, plastic vials made from high density polyethylene may be used.

[0087] The supports having the deposits thereon may be separated from the solvent portion by any appropriate method such as filtration, evaporation (e.g., by spray-drying), sublimation (e.g., freeze-drying), or a combination
25 thereof. The evaporation or sublimation rate may be enhanced by adding heat (e.g., raising the temperature of the solvent) and/or decreasing the atmospheric pressure to which the solvent is exposed.

[0088] In one embodiment a frozen or solidified suspension is freeze-dried to remove the solvent portion therefrom. The freeze-drying may be carried
30 out in any appropriate apparatus, such as a LABCONCO FREEZE DRY SYSTEM (Model 79480). Intuitively, one of skill in the art would typically maintain the temperature of the frozen suspension below the melting point of the solvent (i.e., the solvent is removed by sublimation), in order to prevent agglomeration of the supports. The freeze-drying method described or
35 illustrated herein may be carried out under such conditions. Surprisingly, however, it is not critical that the solvent portion remain fully frozen. Specifically, it has been discovered that a free-flowing, non-agglomerated powder may be prepared even if the solvent is allowed to melt, provided that the pressure within

the freeze-dryer is maintained at a level that the evaporation rate of the liquid solvent is faster than the melting rate (e.g., below about 0.2 mbar, 0.000197 atm, or 20 Pa). Thus, there is typically not enough solvent in the liquid state to result in agglomeration of the supports. Advantageously, this can be used to
5 decrease the time needed to remove the solvent portion. Removing the solvent portion results in a free-flowing, non-agglomerated supported powder that comprises the supports/particulate support and deposits comprising one or more metal species or precipitated metals on the supports/particulate support.

[0089] To accomplish the conversion of the deposited compound(s) to
10 the desired form of the metal(s) therein, the support and deposited compound(s) are typically heated in a reducing atmosphere (e.g., an atmosphere containing hydrogen and/or an inert gas such as argon) at a temperature sufficient to decompose the deposited compound(s). The temperature reached during the thermal treatment is typically at least as high as the decomposition
15 temperature(s) for the deposited compound(s) and not so high as to result in degradation of the supports and agglomeration of the supports and/or the deposits. Typically, the temperature is between about 60 °C and about 1100 °C, between about 100 and about 1000 °C, between about 200 and about 800 °C, or between about 400 and about 600 °C. Inorganic metal-containing
20 compounds typically decompose at temperatures between about 600 and 1000 °C.

[0090] The duration of the heat treatment is typically at least sufficient to substantially convert the deposited compounds to the desired state. In general, the temperature and time are inversely related (i.e., conversion is accomplished
25 in a shorter period of time at higher temperatures and vice versa). At the temperatures typical for converting the inorganic metal-containing compounds to an alloy set forth above, the duration of the heat treatment is typically at least about 30 minutes (e.g., about 1, 2, 4, 6, 8, 10, 12 hours, 14 hours or longer). For example, the duration may be between about 1 and about 14 hours, about 2
30 and about 12 hours, or between about 4 and about 6 hours.

[0091] In this regard it is to be noted, however, that the particle size of the resulting catalyst composition alloy, or precursor thereto, may additionally or alternatively be controlled by control of the temperature at which the deposited metal-containing compounds are heated, and/or the length of time over which
35 the compounds are maintained at that temperature. For example, in order to obtain a catalyst composition, or catalyst composition precursor, having the size as noted elsewhere herein (e.g., greater than about 10 Å to less than 50 Å, greater than about 15 Å to less than 40 Å, greater than about 20 Å to less than

35 Å, or greater than about 25 Å to less than 30 Å), in one embodiment the deposited compound(s) is(are) heated in a reducing atmosphere to a temperature which is greater than about 450°C and less than 800°C, more preferably greater than about 450°C and less than about 750°C, still more preferably greater than about 525°C and less than about 750°C, and still more preferably greater than about 600°C and less than about 700°C, for a duration sufficient to convert said compounds to an alloy of copper and platinum (e.g., preferably for about 2 to about 14 hours, more preferably for about 6 to about 14 hours, still more preferably for about 6.5 to about 13 hours, and still more preferably for about 7 to about 12 hours). In an alternative embodiment, the deposited compound(s) is(are) heated in a reducing atmosphere to a temperature which is greater than about 750°C and less than 950°C, and more preferably greater than about 800°C and less than about 900°C, for a duration of about 1.5 to about 5 hours, more preferably for about 1.75 to about 4.5 hours, and still more preferably for about 2 to about 4 hours).

[0092] Referring now to Figure 1, a carbon supported catalyst alloy powder particle 1 of the present invention, produced in accordance with the freeze-drying method described or illustrated herein, comprises a carbon support 2 and deposits 3 of the catalyst alloy on the support. A particle and a powder comprising said particles may have a loading that is up to about 90 weight percent. However, when a supported catalyst powder is used as a fuel cell catalyst, the loading is typically between about 5 and about 60 weight percent, and is preferably between about 15 and about 45 or about 55 weight percent, or more preferably between about 20 and about 40 or 50 weight percent (e.g., about 20 weight percent, 45 weight percent, or about 50 weight percent). Increasing the loading to greater than about 60 weight percent does not typically result in an increase in the activity. Without being held to a particular theory, it is believed that excess loading covers a portion of the deposited metal and the covered portion cannot catalyze the desired electrochemical reaction. On the other hand, the activity of the supported catalyst typically decreases significantly if the loading is below about 5 weight percent.

[0093] The freeze-dry method may be used to produce supported catalyst alloy powders that are heavily loaded with nanoparticle deposits of a catalyst alloy that comprises one or more non-noble metals, wherein the deposits have a relatively narrow size distribution. For example, in one embodiment the supported non-noble metal-containing catalyst alloy powder may have a metal loading of at least about 20 weight percent of the powder, an

average deposit size that is no greater than about 10 nm, and a deposit size distribution in which at least about 70 percent of the deposits are within about 50 and 150 percent of the average deposit size. In another embodiment, the metal loading may preferably be between about 20 and about 60 weight percent, and
5 more preferably between about 20 and about 40 weight percent.

[0094] The freeze-dry method of preparing supported catalyst powders allows for improved control of the stoichiometry of the deposits because the suspension is preferably kept within a single container, the solution is not physically separated from the supports (e.g., by filtration), and freezing results in
10 substantially all of the solute precipitating on the supports. Additionally, the deposits tend to be isolated, small, and uniformly dispersed over the surface of the supports, thereby increasing the overall catalytic activity. Still further, because filtering is not necessary, extremely fine particles are not lost and the supported catalyst powders produced by this method tend to have a greater
15 surface area and activity. Also, the act of depositing the metal species on the supports is fast. For example, immersing a container of the dispersion/suspension in a cryogenic liquid may solidify the dispersion/suspension in about three to four minutes.

4. *Unsupported Catalyst Compositions in Electrode/Fuel Cell Applications*

20 [0095] It is to be noted that, in another embodiment of the present invention, a catalyst composition (e.g., the catalyst composition comprising or consisting essentially of an alloy of the metal components), and/or the precursor thereto, may be unsupported; that is, a catalyst composition as set forth herein may be employed in the absence of support particles. More specifically, it is to
25 be noted that in another embodiment of the present invention a catalyst composition comprising platinum and copper as defined herein may be directly deposited (e.g., sputtered) onto, for example: (i) a surface of one or both of the electrodes (e.g., the anode, the cathode or both), and/or (ii) one or both surfaces of a polyelectrolyte membrane, and/or (iii) some other surface, such as a
30 backing for the membrane (e.g., carbon paper).

[0096] In this regard it is to be further noted that each constituent (e.g., metal-containing compound) of the composition may be deposited separately, each for example as a separate layer on the surface of the electrode, membrane, etc. Alternatively, two or more constituents may be deposited at the
35 same time. Additionally, when the composition comprises or consists essentially of an alloy of these metals, the alloy may be formed and then deposited, or the

constituents thereof may be deposited and then the alloy subsequently formed thereon.

[0097] Deposition of the constituent(s) may be achieved using means known in the art, including for example known sputtering techniques (see, e.g., 5 PCT Application No. WO 99/16137, or U.S. Patent No. 6,171,721). Generally speaking, however, in one approach sputter-deposition is achieved by creating, within a vacuum chamber in an inert atmosphere, a voltage differential between a target component material and the surface onto which the target constituent is to be deposited, in order to dislodge particles from the target constituent material 10 which are then attached to the surface of, for example, an electrode or electrolyte membrane, thus forming a coating of the target constituent thereon. In one embodiment, the constituents are deposited on a polymeric electrolyte membrane, including for example (i) a copolymer membrane of tetrafluoroethylene and perfluoropolyether sulfonic acid (such as the membrane 15 material sold under the trademark NAFION™), (ii) a perfluorinated sulfonic acid polymer (such as the membrane material sold under the trademark ACIPLEX), (iii) polyethylene sulfonic acid polymers, (iv) polyketone sulfonic acids, (v) polybenzimidazole doped with phosphoric acid, (vi) sulfonated polyether sulfones, and (vii) other polyhydrocarbon-based sulfonic acid polymers.

20 [0098] It is to be noted that the specific amount of each metal or constituent of the composition may be controlled independently, in order to tailor the composition to a given application. In some embodiments, however, the amount of each deposited constituent, or alternatively the amount of the deposited catalyst (e.g., catalyst alloy), may be less than about 5 mg/cm² of 25 surface area (e.g., electrode surface area, membrane surface area, etc.), less than about 1 mg/cm², less than about 0.5 mg/cm², less than about 0.1 mg/cm², or even less than about 0.05 mg/cm². In other embodiments, the amount of the deposited constituent, or alternatively the amount of the deposited catalyst (e.g., catalyst alloy), may range from about 0.5 mg/cm² to less than about 5 mg/cm², 30 or from about 0.1 mg/cm² to less than about 1 mg/cm².

[0099] It is to be further noted that the specific amount of each constituent, or the composition, and/or the conditions under which the constituent, or composition, are deposited, may be controlled in order to control the resulting thickness of the constituent, or composition, layer on the surface of 35 the electrode, electrolyte membrane, etc. For example, as determined by means known in the art (e.g., scanning electron microscopy or Rutherford back scattering spectrophotometric method), the deposited layer of the constituent or composition may have a thickness ranging from several angstroms (e.g., about

2, 4, 6, 8, 10Å or more) to several tens of angstroms (e.g., about 20, 40, 60, 80, 100Å or more), up to several hundred angstroms (e.g., about 200, 300, 400, 500Å or more). Additionally, after all of the constituents have been deposited, and optionally alloyed (or, alternatively, after the composition has been
5 deposited, and optionally alloyed), the layer of the composition of the present invention may have a thickness ranging from several tens of angstroms (e.g., about 20, 40, 60, 80, 100Å or more), up to several hundred angstroms (e.g., about 200, 400, 600, 800, 1000, 1500Å or more). Thus, in different
10 embodiments the thickness may be, for example, between about 10 and about 500 angstroms (Å), between about 20 and about 200 angstroms (Å), and between about 40 and about 100 angstroms (Å).

[0100] It is to be still further noted that in embodiments wherein a composition (or the constituents thereof) is deposited as a thin film on the surface of, for example, an electrode or electrolyte membrane, the various
15 concentration of platinum and copper therein may be as previously described herein. Additionally, in other embodiments, the concentration of platinum and/or copper in the composition may be other than as previously described.

5. *Incorporation of the Composition in a Fuel Cell*

[0101] The compositions of the present invention are particularly suited
20 for use as catalysts in proton exchange membrane fuel cells. As shown in Figures 2 and 3, a fuel cell, generally indicated at 20, comprises a fuel electrode (anode) 22 and an air electrode/oxidizer electrode (cathode) 23. In between the electrodes 22 and 23, a proton exchange membrane 21 serves as an electrolyte and is usually a strongly acidic ion exchange membrane, such as a
25 perfluorosulphonic acid-based membrane. Preferably, the proton exchange membrane 21, the anode 22, and the cathode 23 are integrated into one body to minimize contact resistance between the electrodes and the proton exchange membrane. Current collectors 24 and 25 engage the anode and the cathode, respectively. A fuel chamber 28 and an air chamber 29 contain the respective
30 reactants and are sealed by sealants 26 and 27, respectively.

[0102] In general, electricity is generated by hydrogen-containing fuel combustion (i.e., the hydrogen-containing fuel and oxygen react to form water, carbon dioxide and electricity). This is accomplished in the above-described fuel cell by introducing the hydrogen-containing fuel F into the fuel chamber 28, while
35 oxygen O (preferably air) is introduced into the air chamber 29, whereby an electric current can be immediately transferred between the current collectors 24

and 25 through an outer circuit (not shown). Ideally, the hydrogen-containing fuel is oxidized at the anode 22 to produce hydrogen ions, electrons, and possibly carbon dioxide gas. The hydrogen ions migrate through the strongly acidic proton exchange membrane 21 and react with oxygen and electrons transferred through the outer circuit to the cathode 23 to form water. If the hydrogen-containing fuel F is methanol, it is preferably introduced as a dilute acidic solution to enhance the chemical reaction, thereby increasing power output (e.g., a 0.5 M methanol/0.5 M sulfuric acid solution).

[0103] To prevent the loss of ionic conduction in the proton exchange membranes, these typically remain hydrated during operation of the fuel cell. As a result, the material of the proton exchange membrane is typically selected to be resistant to dehydration at temperatures up to between about 100 and about 120 °C. Proton exchange membranes usually have reduction and oxidation stability, resistance to acid and hydrolysis, sufficiently low electrical resistivity (e.g., $<10 \Omega \cdot \text{cm}$), and low hydrogen or oxygen permeation. Additionally, proton exchange membranes are usually hydrophilic. This ensures proton conduction (by reversed diffusion of water to the anode), and prevents the membrane from drying out thereby reducing the electrical conductivity. For the sake of convenience, the layer thickness of the membranes is typically between 50 and 200 μm . In general, the foregoing properties are achieved with materials that have no aliphatic hydrogen-carbon bonds, which, for example, are achieved by replacing hydrogen with fluorine or by the presence of aromatic structures; the proton conduction results from the incorporation of sulfonic acid groups (high acid strength). Suitable proton-conducting membranes also include perfluorinated sulfonated polymers such as NAFIONTM and its derivatives produced by E.I. du Pont de Nemours & Co., Wilmington, Delaware. NAFIONTM is based on a copolymer made from tetrafluoroethylene and perfluorovinylether, and is provided with sulfonic groups working as ion-exchanging groups. Other suitable proton exchange membranes are produced with monomers such as perfluorinated compounds (e.g., octafluorocyclobutane and perfluorobenzene), or even monomers with C-H bonds that do not form any aliphatic H atoms in a plasma polymer, which could constitute attack sites for oxidative breakdown.

[0104] The electrodes of the present invention comprise the catalyst compositions of the present invention and an electrode substrate upon which the catalyst is deposited. In one embodiment, the composition is directly deposited on the electrode substrate. In another embodiment, the composition is supported on electrically conductive supports and the supported composition is deposited on the electrode substrate. The electrode may also comprise a

proton conductive material that is in contact with the composition. The proton conductive material may facilitate contact between the electrolyte and the composition, and may thus enhance fuel cell performance. Preferably, the electrode is designed to increase cell efficiency by enhancing contact between
5 the reactant (i.e., fuel or oxygen), the electrolyte and the composition. In particular, porous or gas diffusion electrodes are typically used since they allow the fuel/oxidizer to enter the electrode from the face of the electrode exposed to the reactant gas stream (back face), and the electrolyte to penetrate through the face of the electrode exposed to the electrolyte (front face), and reaction
10 products, particularly water, to diffuse out of the electrode.

[0105] Preferably, the proton exchange membrane, electrodes, and catalyst composition are in contact with each other. This is typically accomplished by depositing the composition either on the electrode, or on the proton exchange membrane, and then placing the electrode and membrane in
15 contact. The composition of this invention can be deposited on either the electrode or the membrane by a variety of methods, including plasma deposition, powder application (the powder may also be in the form of a slurry, a paste, or an ink), chemical plating, and sputtering. Plasma deposition generally entails depositing a thin layer (e.g., between 3 and 50 μm , preferably between 5
20 and 20 μm) of a catalyst composition on the membrane using low-pressure plasma. By way of example, an organic platinum compound such as trimethylcyclopentadienyl-platinum is gaseous between 10^{-4} and 10 mbar and can be excited using radio-frequency, microwaves, or an electron cyclotron resonance transmitter to deposit platinum on the membrane. According to
25 another procedure, a catalyst powder, for example, is distributed onto the proton exchange membrane surface and integrated at an elevated temperature under pressure. If, however, the amount of catalyst powder exceeds about 2 mg/cm^2 , the inclusion of a binder such as polytetrafluoroethylene is common. Further, the catalyst may be plated onto dispersed small support particles (e.g., the size
30 is typically between 20 and 200 \AA , and more preferably between about 20 and 100 \AA). This increases the catalyst surface area, which in turn increases the number of reaction sites leading to improved cell efficiency. In one such chemical plating method, for example, a powdery carrier material such as conductive carbon black is contacted with an aqueous solution or aqueous
35 suspension (slurry) of compounds of metallic components constituting the alloy to permit adsorption or impregnation of the metallic compounds or their ions on or in the carrier. Then, while the slurry is stirred at high speed, a dilute solution of suitable fixing agent such as ammonia, hydrazine, formic acid, or formalin is

slowly added drop-wise to disperse and deposit the metallic components on the carrier as insoluble compounds or partly reduced fine metal particles.

[0106] The loading, or surface concentration, of a composition on the membrane or electrode is based in part on the desired power output and cost for a particular fuel cell. In general, power output increases with increasing concentration; however, there is a level beyond which performance is not improved. Likewise, the cost of a fuel cell increases with increasing concentration. Thus, the surface concentration of composition is selected to meet the application requirements. For example, a fuel cell designed to meet the requirements of a demanding application such as an extraterrestrial vehicle will usually have a surface concentration of the composition sufficient to maximize the fuel cell power output. For less demanding applications, economic considerations dictate that the desired power output be attained with as little of the composition as possible. Typically, the loading of composition is between about 0.01 and about 6 mg/cm². Experimental results to-date indicate that in some embodiments the composition loading is preferably less than about 1 mg/cm², and more preferably between about 0.1 and 1 mg/cm².

[0107] To promote contact between the collector, electrode, composition and membrane, the layers are usually compressed at high temperature. The housings of the individual fuel cells are configured in such a way that a good gas supply is ensured, and at the same time the product water can be discharged properly. Typically, several fuel cells are joined to form stacks, so that the total power output is increased to economically feasible levels.

[0108] In general, the catalyst compositions and fuel cell electrodes of the present invention may be used to electrocatalyze any fuel containing hydrogen (e.g., hydrogen and reformed-hydrogen fuels). Also, hydrocarbon-based fuels may be used including: saturated hydrocarbons, such as methane (natural gas), ethane, propane and butane; garbage off-gas; oxygenated hydrocarbons, such as methanol and ethanol; fossil fuels, such as gasoline and kerosene; and, mixtures thereof.

[0109] To achieve the full ion-conducting property of proton exchange membranes, in some embodiments suitable acids (gases or liquids) are typically added to the fuel. For example, SO₂, SO₃, sulfuric acid, trifluoromethanesulfonic acid or the fluoride thereof, also strongly acidic carboxylic acids such as trifluoroacetic acid, and volatile phosphoric acid compounds may be used ("Ber. Bunsenges. Phys. Chem.", Volume 98 (1994), pages 631 to 635).

6. *Fuel Cell Uses*

[0110] As set forth above, the compositions of the present invention are useful as catalysts in fuel cells that generate electrical energy to perform useful work. For example, the compositions may be used in fuel cells which are in:

5 electrical utility power generation facilities; uninterrupted power supply devices; extraterrestrial vehicles; transportation equipment, such as heavy trucks, automobiles, and motorcycles (see, Fuji et al., U.S. Pat. No. 6,048,633; Shinkai et al., U.S. Pat. No. 6,187,468; Fuji et al., U.S. Pat. No. 6,225,011; and Tanaka et al., U.S. Pat. No. 6,294,280); residential power generation systems; mobile

10 communications equipment such as wireless telephones, pagers, and satellite phones (see, Prat et al., U.S. Pat. No. 6,127,058 and Kelley et al., U.S. Pat. No. 6,268,077); mobile electronic devices such as laptop computers, personal data assistants, audio recording and/or playback devices, digital cameras, digital video cameras, and electronic game playing devices; military and aerospace

15 equipment such as global positioning satellite devices; and, robots.

7. *Definitions*

[0111] Activity is defined as the maximum sustainable, or steady state, current (Amps) obtained from the electrocatalyst, when fabricated into an electrode, at a given electric potential (Volts). Additionally, because of

20 differences in the geometric area of electrodes, when comparing different electrocatalysts, activity is often expressed in terms of current density (A/cm^2).

[0112] An alloy may be described as a solid solution in which the solute and solvent atoms (the term solvent is applied to the metal that is in excess) are arranged at random, much in the same way as a liquid solution may be

25 described. If some solute atoms replace some of those of the solvent in the structure of the latter, the solid solution may be defined as a substitutional solid solution. Alternatively, an interstitial solid solution is formed if a smaller atom occupies the interstices between the larger atoms. Combinations of the two types are also possible. Furthermore, in certain solid solutions, some level of

30 regular arrangement may occur under the appropriate conditions resulting in a partial ordering that may be described as a superstructure. If long-range ordering of atoms occurs, the alloy may be described as crystallographically ordered, or simply ordered. These alloys may have characteristics that may be distinguishable through characterization techniques such as XRD. Significant

35 changes in XRD may be apparent due to changes in symmetry. Although the

global arrangement of the metal atoms may be similar in the case of a solid solution and an ordered alloy, the relationship between the specific locations of the metal A and metal B atoms is now ordered, not random, resulting in different diffraction patterns. Further, a homogeneous alloy is a single compound
5 comprising the constituent metals. A heterogeneous alloy comprises an intimate mixture of individual metals and/or metal-containing compounds. An alloy, as defined herein, is also meant to include materials which may comprise elements which are generally considered to be non-metallic. For example, some alloys of the present invention may comprise oxygen and/or carbon in an amount that is
10 generally considered to be a low or impurity level (see, e.g., Structural Inorganic Chemistry, A.F. Wells, Oxford University Press, 5th Edition, 1995, chapter 29).

8. EXAMPLES

Example 1 - Forming Catalysts Compositions on Individually Addressable Electrodes

15 **[0113]** The catalyst compositions set forth in Tables A-O, infra, were prepared using the combinatorial techniques disclosed in Warren et al., U.S. Pat. No. 6,187,164; Wu et al., U.S. Pat. No. 6,045,671; Strasser, P., Gorer, S. and Devenney, M., *Combinatorial Electrochemical Techniques For The Discovery of New Fuel-Cell Cathode Materials*, Nayayanan, S.R., Gottesfeld, S.
20 and Zawodzinski, T., eds., *Direct Methanol Fuel Cells*, Proceedings of the Electrochemical Society, New Jersey, 2001, p. 191; and Strasser, P., Gorer, S. and Devenney, M., *Combinatorial Electrochemical Strategies For The Discovery of New Fuel-Cell Electrode Materials*, Proceedings of the International Symposium on Fuel Cells for Vehicles, 41st Battery Symposium, The
25 Electrochemical Society of Japan, Nagoya 2000, p. 153. For example, an array of independent electrodes (with areas of between about 1 and 3 mm²) was fabricated on inert substrates (e.g., glass, quartz, sapphire, alumina, plastics, and thermally treated silicon). The individual electrodes were located substantially in the center of the substrate, and were connected to contact pads
30 around the periphery of the substrate with wires. The electrodes, associated wires, and contact pads were fabricated from a conducting material (e.g., titanium, gold, silver, platinum, copper or other commonly used electrode materials).

[0114] Specifically, the catalyst compositions set forth in Tables A-O were prepared using a photolithography/RF magnetron sputtering technique (GHz range) to deposit a thin film of the catalysts on arrays of 64 individually addressable electrodes. A quartz insulating substrate was provided and
5 photolithographic techniques were used to design and fabricate the electrode patterns on it. By applying a predetermined amount of photoresist to the substrate, photolyzing pre-selected regions of the photoresist, removing those regions that have been photolyzed (e.g., by using an appropriate developer), depositing a layer of titanium about 500 nm thick using RF magnetron sputtering
10 over the entire surface and removing predetermined regions of the deposited titanium (e.g. by dissolving the underlying photoresist), intricate patterns of individually addressable electrodes were fabricated on the substrate.

[0115] Referring to Figure 4, the fabricated array 40 consisted of 64 individually addressable electrodes 41 (about 1.7 mm in diameter) arranged in
15 an 8 x 8 square that were isolated from each other (by adequate spacing) and from the substrate 44 (fabricated on an insulating substrate), and whose interconnects 42 and contact pads 43 were insulated from the electrochemical testing solution (by hardened photoresist or other suitable insulating material).

[0116] After the initial array fabrication and prior to deposition of the
20 catalysts for screening, a patterned insulating layer covering the wires and an inner portion of the peripheral contact pads was deposited, leaving the electrodes and the outer portion of the peripheral contact pads exposed (preferably approximately half of the contact pad is covered with this insulating layer). Because of the insulating layer, it is possible to connect a lead (e.g., a
25 pogo pin or an alligator clip) to the outer portion of a given contact pad and address its associated electrode while the array is immersed in solution, without having to worry about reactions that can occur on the wires or peripheral contact pads. The insulating layer was a hardened photoresist, but any other suitable material known to be insulating in nature could have been used (e.g., glass,
30 silica, alumina, magnesium oxide, silicon nitride, boron nitride, yttrium oxide, or titanium dioxide).

[0117] Following the creation of the titanium electrode array, a steel mask having 64 holes (1.7 mm in diameter) was pressed onto the substrate to prevent deposition of sputtered material onto the insulating resist layer. The
35 deposition of the catalyst was also accomplished using RF magnetron sputtering and a two shutter masking system as described by Wu et al. which enable the deposition of material onto 1 or more electrodes at a time. Each individual thin film catalyst was created by a super lattice deposition method. For example,

when preparing a catalyst composition consisting essentially of metals M1 and M2, each is deposited onto an electrode, and partially or fully alloyed with the other metals thereon. More specifically, first a metal M1 sputter target is selected and a thin film of M1 having a defined thickness is deposited on the electrode. This initial thickness is typically from about 3 to about 12 Å. After this, metal M2 is selected as the sputter target and a layer of M2 is deposited onto the layer of M1. The thickness of M2 layer is also from about 3 to about 12 Å. The thicknesses of the deposited layers are in the range of the diffusion length of the metal atoms (e.g., about 10 to about 30 Å), which allows in-situ alloying of the metals to form a M1-M2 alloy film. As a result of the two deposition steps, an alloy thin film (6 - 25 Å thickness) of the desired stoichiometry is created. This concludes one deposition cycle. In order to achieve the desired total thickness of a catalyst composition, deposition cycles are repeated as necessary which results in the creation of a super-lattice structure of a defined total thickness (typically about 700 Å). Although the number, thickness (stoichiometry) and order of application of the individual metal layers may be determined manually, it is desirable to utilize a computer program to design an output file which contains the information necessary to control the operation of the sputtering device during the preparation of a particular library wafer (i.e., array). One such computer program is the LIBRARY STUDIO software available from Symyx Technologies, Inc. of Santa Clara, California and described in European Patent No. 1080435 B1. The compositions of several as-sputtered alloys were analyzed using Electron Dispersive Spectroscopy (EDS) to confirm that they were consistent with desired compositions (chemical compositions determined using EDS are within about 5% of the actual composition).

[0118] Arrays were prepared to evaluate the specific alloy compositions set forth in Tables A1-A10 and B-O, below. For the arrays of Tables A1-A10 and B-G, each had one electrode that consisted essentially of platinum, which served as an internal standard for the screening of the alloys on that array. For the arrays of Tables H-O, an internal platinum standard electrode was not present. Rather, these samples were evaluated against an external platinum standard comprising an array of 64 platinum electrodes (to determine the experimental error of the oxygen reduction test) in which the oxygen reduction activity of the 64 platinum electrodes averaged -0.75 mA/cm^2 at $+0.1 \text{ V}$ vs. a mercury/mercury sulfate electrode.

Table A1

Array Number	Electrode Number	End Current Density (Absolute Activity) mA/cm ²	End Current Density per Weight Fraction of Pt mA/cm ²	Relative Activity Compared to Internal Pt	Pt	Cu	
					atomic %	atomic %	
5	133379	6	-0.48	-0.59	1.62	60	40
	133379	27	-0.37	-0.49	1.24	50	50
	133379	30	-0.12	-0.27	0.40	20	80

Table A2

Array Number	Electrode Number	End Current Density (Absolute Activity) mA/cm ²	End Current Density per Weight Fraction of Pt mA/cm ²	Relative Activity Compared to Internal Pt	Pt	Cu	
					atomic %	atomic %	
10	133802	8	-1.17	-1.43	1.58	60	40
	133802	35	-1.04	-1.47	1.41	44	56
	133802	40	-0.89	-0.97	1.21	80	20
	133802	51	-0.89	-1.04	1.20	67	33
	133802	3	-0.47	-1.01	0.64	22	78

15

Table A3

20	Array Number	Electrode Number	End Current Density (Absolute Activity) mA/cm ²	End Current Density per Weight Fraction of Pt mA/cm ²	Relative Activity Compared to Internal Pt	Pt	Cu
						atomic %	atomic %
	132991	27	-0.93	-1.23	1.55	50	50
	132991	6	-0.79	-0.96	1.32	60	40
	132991	30	-0.23	-0.52	0.38	20	80

Table A4

Array Number	Electrode Number	End Current Density (Absolute Activity) mA/cm ²	End Current Density per Weight Fraction of Pt mA/cm ²	Relative Activity Compared to Internal Pt	Pt	Cu	
					atomic %	atomic %	
25	134165	55	-1.41	-1.71	1.45	60	40
	134165	64	-1.37	-1.67	1.42	60	40
	134165	63	-0.05	-0.11	0.05	20	80

Table A5

Array Number	Electrode Number	End Current Density (Absolute Activity) mA/cm ²	End Current Density per Weight Fraction of Pt mA/cm ²	Relative Activity Compared to Internal Pt	Pt	Cu	
					atomic %	atomic %	
5	126556	6	-0.15	-0.18	1.44	60	40
	126556	27	-0.13	-0.17	1.22	50	50
	126556	30	-0.05	-0.12	0.50	20	80

Table A6

Array Number	Electrode Number	End Current Density (Absolute Activity) mA/cm ²	End Current Density per Weight Fraction of Pt mA/cm ²	Relative Activity Compared to Internal Pt	Pt	Cu	
					atomic %	atomic %	
10	130758	8	-1.24	-1.51	1.39	60	40
	130758	35	-1.15	-1.62	1.29	44	56
	130758	51	-0.92	-1.07	1.03	67	33
	130758	40	-0.88	-0.95	0.99	80	20

Table A7

15

Array Number	Electrode Number	End Current Density (Absolute Activity) mA/cm ²	End Current Density per Weight Fraction of Pt mA/cm ²	Relative Activity Compared to Internal Pt	Pt	Cu
					atomic %	atomic %
132971	27	-1.00	-1.32	1.34	50	50
132971	6	-0.87	-1.06	1.17	60	40
132971	30	-0.17	-0.38	0.22	20	80

Table A8

Array Number	Electrode Number	End Current Density (Absolute Activity) mA/cm ²	End Current Density per Weight Fraction of Pt mA/cm ²	Relative Activity Compared to Internal Pt	Pt	Cu	
					atomic %	atomic %	
25	133815	35	-0.71	-1.00	1.08	45	55
	133815	51	-0.70	-0.81	1.06	67	33
	133815	8	-0.67	-0.82	1.02	60	40
	133815	40	-0.64	-0.69	0.97	80	20
	133815	3	-0.10	-0.21	0.15	22	78

Table A9

Array Number	Electrode Number	End Current Density (Absolute Activity) mA/cm ²	End Current Density per Weight Fraction of Pt mA/cm ²	Relative Activity Compared to Internal Pt	Pt	Cu	
					atomic %	atomic %	
5	133352	35	-0.81	-1.14	1.03	44	56
	133352	51	-0.79	-0.92	1.01	67	33
	133352	8	-0.73	-0.89	0.93	60	40
	133352	40	-0.72	-0.78	0.92	80	20
	133352	3	-0.37	-0.79	0.47	22	78

Table A10

10	Array Number	Electrode Number	End Current Density (Absolute Activity) mA/cm ²	End Current Density per Weight Fraction of Pt mA/cm ²	Relative Activity Compared to Internal Pt	Pt	Cu
						atomic %	atomic %
15	133803	40	-0.81	-0.88	1.07	80	20
	133803	35	-0.78	-1.09	1.02	44	56
	133803	51	-0.76	-0.88	1.00	67	33
	133803	8	-0.74	-0.90	0.98	60	40
	133803	3	-0.10	-0.20	0.13	22	78

Table B

	Array Number	Electrode Number	End Current Density (Absolute Activity) mA/cm ²	End Current Density per Weight Fraction of Pt mA/cm ²	Relative Activity Compared to Internal Pt	Pt atomic %	Cu atomic %
20	136300*	1	-4.05	-7.30	6.46	29	71
	136300*	2	-3.83	-6.52	6.11	32	68
	136300*	3	-3.20	-5.13	5.11	35	65
	136300*	4	-2.02	-3.04	3.23	39	61
25	136299	1	-1.16	-2.10	1.35	29	71
	136299	2	-1.14	-1.95	1.33	32	68
	136300*	7	-0.79	-0.95	1.26	62	38
	136300*	5	-0.74	-1.04	1.19	45	55
	136300*	6	-0.74	-0.97	1.19	52	48
	137656	49	-0.58	-0.71	1.17	60	40
30	136299	3	-0.98	-1.57	1.14	35	65
	137564	49	-0.62	-0.76	1.10	60	40
	136299	7	-0.93	-1.12	1.08	62	38
	136299	4	-0.92	-1.38	1.07	39	61
	136299	5	-0.90	-1.26	1.04	45	55
35	136299	6	-0.90	-1.17	1.04	52	48
	137674	49	-0.24	-0.30	0.80	60	40

* Array 136300 was heated to about 400 °C for about 12 hours in vacuum prior to being screened in attempts to mimic powder synthesis.

Table C
[Lib. 139107]

	Electrode Number	End Current Density (Absolute Activity)	End Current Density per Weight Fraction of Pt	Relative Activity Compared to Internal Pt	Pt	Cu
		mA/cm ²	mA/cm ²		atomic %	atomic %
5	31	-4.33	-9.96	6.40	20	80
	23	-1.25	-2.19	1.84	30	70
	55	-0.86	-1.29	1.28	40	60
	28	-0.85	-1.27	1.26	40	60
10	56	-0.83	-0.86	1.22	90	10
	50	-0.70	-0.79	1.03	70	30
	47	-0.69	-0.91	1.02	50	50
	26	-0.69	-0.91	1.01	50	50
	42	-0.68	-0.74	1.01	80	20
	48	-0.68	-0.68	1.00	100	0
15	20	-0.67	-0.89	1.00	50	50
	52	-0.67	-0.82	1.00	60	40
	44	-0.64	-0.73	0.95	70	30
	18	-0.63	-0.76	0.93	60	40
20	24	-0.62	-0.67	0.92	80	20
	32	-0.61	-0.69	0.90	70	30

Table D
[Lib. 140044]

	Electrode Number	End Current Density (Absolute Activity)	End Current Density per Weight Fraction of Pt	Relative Activity Compared to Internal Pt	Pt	Cu
		mA/cm ²	mA/cm ²		atomic %	atomic %
25	23	-1.81	-3.19	3.16	30	70
	42	-0.81	-0.88	1.42	80	20
	24	-0.78	-0.84	1.35	80	20
	56	-0.70	-0.72	1.21	90	10
30	44	-0.68	-0.78	1.19	70	30
	52	-0.67	-0.82	1.17	60	40
	18	-0.64	-0.77	1.11	60	40
	47	-0.62	-0.82	1.07	50	50
35	50	-0.61	-0.70	1.07	70	30
	32	-0.60	-0.69	1.05	70	30
	48	-0.57	-0.57	1.00	100	0
	20	-0.55	-0.74	0.97	50	50
40	26	-0.53	-0.70	0.91	50	50
	28	-0.49	-0.72	0.85	40	60
	55	-0.47	-0.70	0.82	40	60

Table E
[Lib. 140150]

	Electrode Number	End Current Density (Absolute Activity)	End Current Density per Weight Fraction of Pt	Relative Activity Compared to Internal Pt	Pt	Cu
		mA/cm ²	mA/cm ²		atomic %	atomic %
5	23	-2.59	-4.56	2.05	30	70
	31	-2.06	-4.74	1.63	20	80
	55	-1.52	-2.26	1.20	40	60
	28	-1.51	-2.24	1.19	40	60
10	26	-1.40	-1.86	1.11	50	50
	47	-1.39	-1.84	1.10	50	50
	56	-1.36	-1.41	1.08	90	10
	42	-1.36	-1.47	1.08	80	20
	20	-1.35	-1.79	1.07	50	50
15	52	-1.35	-1.64	1.07	60	40
	24	-1.29	-1.40	1.02	80	20
	48	-1.26	-1.26	1.00	100	0
	32	-1.26	-1.43	1.00	70	30
	18	-1.23	-1.50	0.98	60	40
20	44	-1.20	-1.36	0.95	70	30
	50	-1.19	-1.36	0.94	70	30

Table F
[Lib. 141101]

	Electrode Number	End Current Density (Absolute Activity)	End Current Density per Weight Fraction of Pt	Relative Activity Compared to Internal Pt	Pt	Cu
		mA/cm ²	mA/cm ²		atomic %	atomic %
25	23	-2.13	-3.74	26.65	30	70
	28	-0.43	-0.63	5.35	40	60
	55	-0.39	-0.58	4.92	40	60
	47	-0.32	-0.42	3.99	50	50
	24	-0.28	-0.30	3.50	80	20
30	26	-0.27	-0.36	3.41	50	50
	20	-0.26	-0.34	3.26	50	50
	50	-0.25	-0.29	3.14	70	30
	42	-0.23	-0.25	2.92	80	20
	44	-0.22	-0.26	2.81	70	30
35	52	-0.22	-0.26	2.71	60	40
	32	-0.22	-0.25	2.70	70	30
	18	-0.21	-0.25	2.58	60	40
	56	-0.19	-0.20	2.43	90	10
	48	-0.08	-0.08	1.00	100	0

Table G
[Lib. 141477]

	Electrode Number	End Current Density (Absolute Activity)	End Current Density per Weight Fraction of Pt	Relative Activity Compared to Internal Pt	Pt	Cu
		mA/cm ²	mA/cm ²		atomic %	atomic %
5	48	-4.31	-9.99	2.95	19.82	80.18
	56	-4.24	-9.81	2.90	19.82	80.18
	40	-4.18	-9.68	2.86	19.82	80.18
	64	-3.94	-9.14	2.70	19.82	80.18
10	8	-3.68	-8.54	2.52	19.82	80.18
	16	-3.65	-8.45	2.50	19.82	80.18
	32	-3.32	-7.70	2.28	19.82	80.18
	24	-3.27	-7.58	2.24	19.82	80.18
15	47	-2.71	-5.00	1.85	27.77	72.23
	31	-2.25	-4.15	1.54	27.77	72.23
	39	-2.13	-3.93	1.46	27.77	72.23
	6	-1.92	-3.00	1.32	36.58	63.42
20	14	-1.91	-2.99	1.31	36.58	63.42
	54	-1.90	-2.97	1.30	36.58	63.42
	22	-1.85	-2.89	1.27	36.58	63.42
	46	-1.81	-2.83	1.24	36.58	63.42
25	62	-1.80	-2.81	1.23	36.58	63.42
	30	-1.77	-2.78	1.22	36.58	63.42
	15	-1.74	-3.22	1.20	27.77	72.23
	38	-1.70	-2.67	1.17	36.58	63.42
30	18	-1.61	-1.72	1.11	83.85	16.15
	35	-1.61	-1.84	1.10	69.76	30.24
	23	-1.60	-2.96	1.10	27.77	72.23
	27	-1.60	-1.83	1.10	69.76	30.24
35	7	-1.59	-2.93	1.09	27.77	72.23
	45	-1.59	-2.18	1.09	46.38	53.62
	43	-1.58	-1.80	1.08	69.76	30.24
	37	-1.57	-2.16	1.08	46.38	53.62
40	55	-1.57	-2.89	1.07	27.77	72.23
	51	-1.55	-1.77	1.06	69.76	30.24
	5	-1.54	-2.12	1.06	46.38	53.62
	28	-1.53	-1.90	1.05	57.37	42.63
45	36	-1.53	-1.90	1.05	57.37	42.63
	50	-1.53	-1.62	1.04	83.85	16.15
	19	-1.52	-1.74	1.04	69.76	30.24
	34	-1.52	-1.62	1.04	83.85	16.15
50	13	-1.51	-2.08	1.04	46.38	53.62
	10	-1.51	-1.61	1.04	83.85	16.15
	53	-1.51	-2.08	1.03	46.38	53.62
	44	-1.50	-1.86	1.03	57.37	42.63
55	60	-1.50	-1.86	1.03	57.37	42.63
	20	-1.49	-1.86	1.02	57.37	42.63
	61	-1.49	-2.05	1.02	46.38	53.62
	52	-1.48	-1.84	1.01	57.37	42.63
60	2	-1.47	-1.56	1.01	83.85	16.15
	4	-1.47	-1.82	1.01	57.37	42.63
	11	-1.47	-1.67	1.01	69.76	30.24
	9	-1.46	-1.46	1.00	100	0

Table H
[Lib. 142776]

Electrode Number	End Current Density (Absolute Activity)	End Current Density per Weight Fraction of Pt	Pt	Cu
	mA/cm ²	mA/cm ²	atomic %	atomic %
8	-1.79	-3.54	25.04	74.96
16	-2.07	-4.09	25.04	74.96
24	-1.36	-2.39	30.06	69.94
32	-1.37	-2.41	30.06	69.94
40	-1.10	-1.76	35.07	64.93
48	-1.58	-2.54	35.07	64.93
56	-1.08	-1.60	40.1	59.9
64	-1.27	-1.89	40.1	59.9

Table I
[Lib. 142767]

Electrode Number	End Current Density (Absolute Activity)	End Current Density per Weight Fraction of Pt	Pt	Cu
	mA/cm ²	mA/cm ²	atomic %	atomic %
8	-1.58	-3.13	25.04	74.96
16	-1.40	-2.76	25.04	74.96
24	-0.92	-1.62	30.06	69.94
32	-0.86	-1.52	30.06	69.94
40	-0.69	-1.11	35.07	64.93
48	-0.71	-1.14	35.07	64.93
56	-0.68	-1.01	40.1	59.9
64	-0.68	-1.01	40.1	59.9

Table J
[Lib. 142766]

Electrode Number	End Current Density (Absolute Activity)	End Current Density per Weight Fraction of Pt	Pt	Cu
	mA/cm ²	mA/cm ²	atomic %	atomic %
8	-1.93	-3.82	25.04	74.96
16	-1.42	-2.81	25.04	74.96
24	-1.20	-2.12	30.06	69.94
32	-1.16	-2.04	30.06	69.94
40	-0.89	-1.42	35.07	64.93
48	-0.97	-1.56	35.07	64.93
56	-0.89	-1.32	40.1	59.9
64	-0.86	1.28	40.1	59.9

Table K
[Lib. 142716]

	Electrode Number	End Current Density (Absolute Activity)	End Current Density per Weight Fraction of Pt	Pt	Cu
		mA/cm ²	mA/cm ²	atomic %	atomic %
5	8	-2.81	-5.54	25.04	74.96
	16	-2.73	-5.40	25.04	74.96
	24	-1.25	-2.20	30.06	69.94
	32	-1.25	-2.20	30.06	69.94
	40	-0.95	-1.52	35.07	64.93
10	48	-0.97	-1.55	35.07	64.93
	56	-1.08	-1.60	40.1	59.9
	64	-0.99	-1.47	40.1	59.9

Table L
[Lib. 142715]

	Electrode Number	End Current Density (Absolute Activity)	End Current Density per Weight Fraction of Pt	Pt	Cu
		mA/cm ²	mA/cm ²	atomic %	atomic %
15	8	-1.28	-2.53	25.04	74.96
	16	-1.18	-2.33	25.04	74.96
	24	-0.95	-1.67	30.06	69.94
	32	-0.88	-1.55	30.06	69.94
	40	-0.67	-1.08	35.07	64.93
20	48	-0.71	-1.14	35.07	64.93
	56	-0.64	-0.96	40.1	59.9
	64	-0.73	-1.09	40.1	59.9

Table M
[Lib. 142714]

25	Electrode Number	End Current Density (Absolute Activity)	End Current Density per Weight Fraction of Pt	Pt	Cu
		mA/cm ²	mA/cm ²	atomic %	atomic %
30	8	-1.06	-2.10	25.04	74.96
	16	-1.28	-2.52	25.04	74.96
	24	-1.30	-2.28	30.06	69.94
	32	-1.54	-2.70	30.06	69.94
	40	-0.96	-1.54	35.07	64.93
	48	-1.29	-2.06	35.07	64.93
	56	-0.88	-1.31	40.1	59.9
	64	-0.96	-1.42	40.1	59.9

Table N
[Lib. 142713]

Electrode Number	End Current Density (Absolute Activity)	End Current Density per Weight Fraction of Pt	Pt	Cu
	mA/cm ²	mA/cm ²	atomic %	atomic %
8	-1.28	-2.53	25.04	74.96
16	-1.16	-2.29	25.04	74.96
24	-0.69	-1.21	30.06	69.94
32	-0.86	-1.52	30.06	69.94
40	-0.44	-0.70	35.07	64.93
48	-0.49	-0.78	35.07	64.93
56	-0.40	-0.60	40.1	59.9
64	-0.45	-0.67	40.1	59.9

Table O
[Lib. 142700]

Electrode Number	End Current Density (Absolute Activity)	End Current Density per Weight Fraction of Pt	Pt	Cu
	mA/cm ²	mA/cm ²	atomic %	atomic %
8	-1.22	-2.41	25.04	74.96
16	-1.03	-2.03	25.04	74.96
24	-0.67	-1.18	30.06	69.94
32	-0.75	-1.33	30.06	69.94
40	-0.46	-0.75	35.07	64.93
48	-0.61	-0.97	35.07	64.93
56	-0.52	-0.78	40.1	59.9
64	-0.61	-0.91	40.1	59.9

Example 2 - Screening Alloys for Electrocatalytic Activity

[0119] The catalyst compositions set forth in Tables A1-A10 and B that were synthesized on arrays according to the method set forth in Example 1 were screened for electrochemical reduction of molecular oxygen to water according to Protocol 1 (detailed below), to determine relative electrocatalytic activity against the internal and/or external platinum standard. Additionally, the catalyst compositions set forth in Tables C-O that were synthesized on arrays according to the method set forth in Example 1 were screened for electrochemical reduction of molecular oxygen to water according to Protocol 2 (detailed below), to determine relative electrocatalytic activity.

[0120] In general, the array wafers were assembled into an electrochemical screening cell and a screening device established an electrical contact between the 64 electrode catalysts (working electrodes) and a 64-channel potentiostat used for the screening. Specifically, each wafer array

was placed into a screening device such that all 64 spots were facing upward and a tube cell body that was generally annular and having an inner diameter of about 2 inches (5 cm) was pressed onto the upward facing wafer surface. The diameter of this tubular cell was such that the portion of the wafer with the square electrode array formed the base of a cylindrical volume while the contact pads were outside the cylindrical volume. A liquid ionic solution (i.e., 0.5 M H_2SO_4 aqueous electrolyte) was poured into this cylindrical volume, and a common counter electrode (i.e., platinum gauze) and a common reference electrode (e.g., mercury/mercury sulfate reference electrode (MMS)) were placed into the electrolyte solution to close the electrical circuit.

[0121] A rotator shaft with blades was placed into the electrolyte to provide forced convection-diffusion conditions during the screening. The rotation rate was typically between about 300 to about 400 rpm. Depending on the screening experiment, either argon or pure oxygen was bubbled through the electrolyte during the measurements. Argon served to remove O_2 gas in the electrolyte to simulate O_2 -free conditions used for the initial conditioning of the catalysts. The introduction of pure oxygen served to saturate the electrolyte with oxygen for the oxygen reduction reaction. During the screening, the electrolyte was maintained at 60 °C and the rotation rate was constant.

[0122] Protocol 1: Three groups of tests were performed to screen the activity of the catalysts. The electrolyte was purged with argon for about 20 minutes prior to the electrochemical measurements. The first group of tests comprised cyclic voltammetric measurements while purging the electrolyte with argon. Specifically, the first group of tests comprised:

- a. a potential sweep from open circuit potential (OCP) to about +0.3 V to about -0.63 V and back to about +0.3 V at a rate of about 20 mV/s;
- b. seventy-five consecutive potential sweeps from OCP to about +0.3 V to about -0.7 V and back to about +0.3 V at a rate of about 200 mV/s; and
- c. a potential sweep from OCP to about +0.3 V to about -0.63 V and back to about +0.3 V at a rate of about 20 mV/s.

The shape of the cyclic voltammetric (CV) profile of the internal Pt standard catalyst as obtained in test (c) was compared to an external standard CV profile obtained from a Pt thin film electrode that had been pretreated until a stable CV was obtained. If test (c) resulted in a similar cyclic voltammogram, the first group of experiments was considered completed. If the shape of the cyclic voltammogram of test (c) did not result in the expected standard Pt CV behavior,

tests (b) and (c) were repeated until the Pt standard catalyst showed the desired standard voltammetric profile. In this way, it was ensured that the Pt standard catalyst showed a stable and well-defined oxygen reduction activity in subsequent experiments. The electrolyte was then purged with oxygen for approximately 30 minutes. The following second group of tests was performed while continuing to purge with oxygen:

- a. measuring the open circuit potential (OCP) for a minute; then, the potential was stepped to -0.4 V, held for a minute, and was then swept up to about +0.4 V at a rate of about 10 mV/s;
- 10 b. measuring the OCP for a minute; then applying a potential step from OCP to about +0.1 V while measuring the current for about 5 minutes; and
- 15 c. measuring the OCP for a minute; then applying a potential step from OCP to about +0.2 V while monitoring the current for about 5 minutes.

The third group of tests comprised a repeat of the second group of tests after about one hour from completion of the second group of tests. The electrolyte was continually stirred and purged with oxygen during the waiting period. All the foregoing test voltages are with reference to a mercury/mercury sulfate (MMS) electrode. Additionally, an external platinum standard comprising an array of 64 platinum electrodes was used to monitor the tests to ensure the accuracy and consistency of the oxygen reduction evaluation.

[0123] Protocol 2: Four groups of tests were performed to screen the activity of the catalysts. The first group is a pretreatment process, whereas the other three groups are identical sets of experiments in order to screen the oxygen reduction activity as well as the current electrochemical surface area of the catalysts. The electrolyte was purged with argon for about 20 minutes prior to the electrochemical measurements. The first group of tests comprised cyclic voltammetric measurements while purging the electrolyte with argon.

Specifically, the first group of tests comprised:

- a. a potential sweep from open circuit potential (OCP) to about +0.3 V to about -0.63 V and back to about +0.3 V at a rate of about 20 mV/s;
- 35 b. fifty consecutive potential sweeps from OCP to about +0.3 V to about -0.7 V and back to about +0.3 V at a rate of about 200 mV/s; and
- 30 c. a potential sweep from OCP to about +0.3 V to about -0.63 V and back to about +0.3 V at a rate of about 20 mV/s.

After step (c) of the first group of tests, the electrolyte was purged with oxygen for approximately 30 minutes. Then, the following second group of tests was performed, which comprised a test in an oxygen-saturated solution (i.e., test (a)), followed by a test performed in an Ar-purged (i.e., an oxygen-free solution,

5 test (b)):

- a. in an oxygen-saturated solution, the OCP was measured for a minute; a potential step was then applied from OCP to about -0.4 V; this potential was held for approximately 30 seconds, and then the potential was stepped to about +0.1 V while measuring the current for about 5 minutes; and
- 10 b. after purging the electrolyte with Ar for approximately 30 minutes, a potential sweep was performed from open circuit potential (OCP) to about +0.3 V to about -0.63 V and back to about +0.3 V, at a rate of about 20 mV/s.

15 The third and fourth group of tests comprised a repeat of the second group of tests after completion. All the foregoing test voltages are with reference to a mercury/mercury sulfate (MMS) electrode. Additionally, an external platinum standard comprising an array of 64 platinum electrodes was used to monitor the tests to ensure the accuracy and consistency of the oxygen reduction
20 evaluation.

[0124] The specific catalyst compositions set forth in Tables A1-A10 and B-O were prepared and screened in accordance with the above-described methods of Protocols 1 (Tables A1-A10 and B) or 2 (Tables C-O), and the test results are set forth therein. The screening results in Tables A1-A10 and B are
25 for the third test group (steady state currents at +0.1 V MMS). The screening results in Tables C-G were taken from the oxygen reduction measurements of the fourth group of tests (i.e., the last screening in an oxygen-saturated solution), the Ar-saturated steps serving as an evaluation of additional catalyst-related parameters, such as surface area over time.

30 [0125] The current value reported (End Current Density) is the result of averaging the last three current values of the chronoamperometric test normalized for geometric surface area. It is to be noted, from the results presented in these Tables, that numerous compositions exhibited an oxygen reduction activity which exceeded, for example, the internal platinum standard
35 (see, e.g., the catalyst compositions in Tables A1-A10 and B-F having a "Relative Activity Compared to Internal Pt" in excess of 1.00; see also the catalyst compositions corresponding to Electrode Numbers, for example: 48, 56, 40, 64, 8, 16, 32, 24, 47, 31, 39, 6, 14, 54, 22, 46, 62, 30, 15, 38, 18, 35, 23, 27,

7 and 45 in Table G; internal platinum standards were not present for Tables H-O).

Example 3 - Synthesis of Supported Catalysts

[0126] The synthesis of Pt-Cu catalyst compositions (see Tables P and Q, Target Catalyst Comp., *infra*) on carbon support particles was attempted according to different method conditions, in order to evaluate the performance of the catalysts while in a state that is typically used in fuel cell. To do so, the catalyst component were deposited or precipitated on supported platinum powder (i.e., platinum nanoparticles supported on carbon black particles). Platinum supported on carbon black is commercially available from companies such as Johnson Matthey, Inc., of New Jersey and E-Tek Div. of De-Nora, N.A., Inc., of Somerset, New Jersey. Such supported platinum powder is available with a wide range of platinum loading. The supported platinum powder used in this Example had a nominal platinum loading of about 20 or about 40 percent by weight, a platinum surface area of between about 150 and about 170 m²/g (determined by CO adsorption), a combined carbon and platinum surface area between about 350 and about 400 m²/g (determined by N₂ adsorption), and an average particle size of less than about 0.5 mm (determined by sizing screen).

[0127] The catalyst compositions of Table P and Q (*infra*) were formed on carbon support particles using a freeze-drying precipitation method. The freeze-drying method comprised forming an initial solution comprising the desired metal atoms in the desired concentrations. Each of the supported catalysts was prepared in an analogous manner, with variations in the amounts of metal-containing compounds used therein. For example, to prepare the target Pt₂₅Cu₇₅ catalyst composition (HFC 344), having a final target platinum loading of about 16.2 percent by weight, 0.143 g of Cu(NO₃)₂•3H₂O was dissolved in a vial containing about 5 ml of H₂O. This solution was then introduced into a HDPE vial containing 0.200 g of supported platinum powder, which had a nominal platinum loading of about 19.2 percent by weight, resulting in the formation of a black suspension. The suspension was homogenized by immersing a probe of a BRANSON SONIFIER 150 into the vial and sonicating the mixture for about 90 seconds at a power level of 3. The vial containing the homogenized suspension was then immersed in a liquid nitrogen bath for about 3 minutes to solidify the suspension. The solid suspension was then freeze-

dried for about 24 hours using a LABCONCO FREEZE DRY SYSTEM (Model 79480) to remove the solvent. The tray and the collection coil of the freeze dryer were maintained at about 27°C and about -49°C, respectively, while evacuating the system (the pressure was maintained at about 0.05 mbar).

- 5 During the final 2.5 hrs of the freeze-drying procedure, the shelf heater was set to 40°C. After completing the freeze-drying procedure, the vial contained a powder comprising the supported platinum powder, and the copper deposited thereon.

- [0128] The recovered powders were then subjected to a heat treatment
10 to reduce the constituents therein to their metallic state, and to fully or partially alloy the copper and the platinum on the carbon black particles. The heat treatment comprised heating the powder in a quartz flow furnace with an atmosphere comprising about 6% H₂ and 94% Ar using a temperature profile of room temperature to about 90°C at a rate of about 5°C/min; holding at about
15 90°C for 2 hours; increasing the temperature to about 200°C at a rate of 5°C/minute; holding at about 200°C for two hours; increasing the temperature at a rate of about 5°C/minute to a maximum temperature of, for example, about 500, 600, 700, 800, 900 or 950°C; holding at the maximum for a duration of about 1.2, 2, 3, 5, 7, 10, or even 12 hours (as indicated in Table P and Q); and,
20 the cooling down to room temperature.

- [0129] In order to determine the actual composition of the supported catalysts, the differently prepared catalysts (e.g., by composition variation or by heat treatment variation) were subjected to EDS (Electron Dispersive Spectroscopy) elemental analysis. For this technique, the sample powders were
25 compressed into 6 mm diameter pellets with a thickness of about 1 mm. The target composition and actual composition for certain of the supported catalyst prepared as described herein are set forth in Table P and Q.

Table P

Powder Number	Target Catalyst Comp.	Max Alloying Temp for a duration (°C/hrs)	Actual Catalyst Comp.	Target Pt Loading (wt%)	Measured Pt Loading (wt%)	Pt Mass Activity at +0.15 V MMS (mA/mg Pt)	Relative activity at +0.15 V MMS	Catalyst Mass Activity at +0.15 V MMS (mA/mg)	Lattice parameter (Å)	Approx. particle size (Å)	electro-chemical surface area [cm ²]
10	Pt	-	Pt	37.8	37.8	128.8	1.00	48.7	3.942	19	
287	Pt ₃₅ Cu ₆₅	700 / 7	-	17.2	-	-	3.51	77.7	3.763	23	
290	Pt ₃₅ Cu ₆₅	900 / 2	-	17.2	-	-	2.38	52.8	3.763	33	
344	Pt ₂₅ Cu ₇₅	700 / 7	-	16.2	-	-	3.60	75.2	3.714	26	
345	Pt ₃₀ Cu ₇₀	700 / 7	-	16.7	-	-	2.66	57.3	3.763	26	
346	Pt ₄₀ Cu ₆₀	700 / 7	-	17.5	-	-	2.28	51.3	3.795	25	
347	Pt ₄₅ Cu ₅₅	700 / 7	-	17.8	-	-	2.27	52.0	3.790	23	
360	Pt ₁₆ Cu ₈₄	700 / 7	-	14.3	-	-	3.18	58.6	3.705	34	
361	Pt ₂₀ Cu ₈₀	700 / 7	-	15.2	-	-	2.98	58.4	3.718	28	
362	Pt ₂₅ Cu ₇₅	700 / 7	-	16.0	-	-	3.63	74.8	3.723	27	
363	Pt ₃₀ Cu ₇₀	700 / 7	Pt ₃₅ Cu ₆₅	16.6	15.5	718.1	5.57	111.3	3.738	25	
364	Pt ₃₅ Cu ₆₅	700 / 7	-	17.0	-	-	3.34	73.2	3.765	23	
365	Pt ₄₀ Cu ₆₀	700 / 7	-	17.4	-	-	3.42	76.6	3.783	22	
367	Pt ₁₆ Cu ₈₄	600 / 7	-	14.3	-	-	3.77	69.5	3.702	31	
368	Pt ₂₀ Cu ₈₀	600 / 7	-	15.2	-	-	3.56	69.6	3.708	28	
369	Pt ₂₅ Cu ₇₅	600 / 7	Pt ₂₈ Cu ₇₁	16.0	14.8	683.0	5.30	101.1	3.722	26	
370	Pt ₃₀ Cu ₇₀	600 / 7	-	16.6	-	-	4.36	93.2	3.738	24	
371	Pt ₃₅ Cu ₆₅	600 / 7	-	17.0	-	-	4.52	98.9	3.763	23	
372	Pt ₄₀ Cu ₆₀	600 / 7	-	17.4	-	-	4.11	92.1	3.784	22	

374	Pt ₂₅ Cu ₇₅	600 / 7	-	-	14.5	-	-	-	4.18	78.0	3.783	17	
375	Pt ₃₀ Cu ₇₀	600 / 7	-	-	15.0	-	-	-	3.83	73.9	3.785	17	
376	Pt ₂₅ Cu ₇₅	600 / 7	-	-	25.0	-	-	-	1.92	62.0	3.756	27	
377	Pt ₃₀ Cu ₇₀	600 / 7	-	-	26.4	-	-	-	1.36	46.3	3.732	29	
378	Pt ₂₅ Cu ₇₅	500 / 7	-	-	14.5	-	-	-	2.29	42.9	3.793	16	
379	Pt ₃₀ Cu ₇₀	500 / 7	-	-	15.0	-	-	-	1.88	36.4	3.811	15	
380	Pt ₂₅ Cu ₇₅	500 / 7	-	-	25.0	-	-	-	0.88	28.3	3.743	33	
381	Pt ₃₀ Cu ₇₀	500 / 7	-	-	26.4	-	-	-	1.46	49.5	3.765	29	
382	Pt ₂₅ Cu ₇₅	600 / 7	Pt ₃₀ Cu ₇₀	15.1	16.0	15.1	721.5	5.60	5.60	108.9	3.729	23	1.05
383	Pt _{27.5} Cu _{72.5}	600 / 7	Pt ₃₂ Cu ₆₈	15.1	16.5	15.1	780.8	6.06	6.06	117.9	3.730	23	
384	Pt ₃₀ Cu ₇₀	600 / 7	-	-	16.6	-	-	4.08	4.08	87.2	3.744	24	
385	Pt _{32.5} Cu _{67.5}	600 / 7	-	-	16.8	-	-	3.53	3.53	76.5	3.760	21	
386	Pt ₃₅ Cu ₆₅	600 / 7	-	-	17.0	-	-	3.61	3.61	79.1	3.770	24	
387	Pt ₂₅ Cu ₇₅	700 / 7	-	-	16.0	-	-	4.24	4.24	87.4	3.732	24	
388	Pt _{27.5} Cu _{72.5}	700 / 7	-	-	16.5	-	-	3.48	3.48	74.0	3.734	26	
389	Pt ₃₀ Cu ₇₀	700 / 7	-	-	16.6	-	-	4.45	4.45	95.2	3.742	27	
390	Pt _{32.5} Cu _{67.5}	700 / 7	-	-	16.8	-	-	4.07	4.07	88.2	3.764	23	
391	Pt ₃₅ Cu ₆₅	700 / 7	-	-	17.0	-	-	3.75	3.75	82.2	3.776	25	

Table Q

Powder Number	Target Catalyst Comp.	Target Pt Loading (wt%)	Max Alloying Temp for a duration (°C/hrs)	Actual Catalyst Comp. before screening	Actual Pt Loading before screening (EDS) (wt%)	Actual Catalyst Comp. after screening	Pt Loading after screening (wt%)	Pt comp. change (%)	Pt Mass Activity at +0.15 V MMS (mA/mg Pt)	Relative activity at +0.15 V MMS	Catalyst Mass Activity at +0.15 V MMS (mA/mg)	EDS Corrected Relative Activity at +0.15 V MMS	Lattice parameter (Å)	Approx. particle size (Å)	Electrochemical surface area [cm ²]
10	Pt	37.8	-	Pt	37.8		-	-	128.82	1.00	48.70	48.70	3.942	19	
398	Pt ₂₅ Cu ₇₅	16.2	600 / 12	Pt ₃₀ Cu ₇₀	15.9		-	-	617.29	4.79	98.77	4.82	3.742	29	
399	Pt ₂₅ Cu ₇₅	16.2	600 / 12	Pt ₂₉ Cu ₇₁	16.4		-	-	516.80	4.01	82.69	3.91	-		
400	Pt ₂₅ Cu ₇₅	16.2	600 / 12	Pt ₃₀ Cu ₇₀	15.9		-	-	635.46	4.93	101.67	4.96	3.742	24	
401	Pt ₂₅ Cu ₇₅	16.2	600 / 12	Pt ₃₀ Cu ₇₀	15.9		-	-	619.48	4.81	99.12	4.84	3.746	24	
421	Pt ₂₅ Cu ₇₅	16.2	600 / 12	-	-		-	-	601.40	4.67	96.22	-	3.753	24	
421	Pt ₂₅ Cu ₇₅	16.2	600 / 12	-	-		-	-	848.18	4.66	135.71	-	3.753	24	
422	Pt ₂₅ Cu ₇₅	16.2	600 / 12	-	-		-	-	-	-	-	-	-	-	
433	Pt ₃₀ Cu ₇₀	16.6	900 / 1.2	Pt ₃₇ Cu ₆₃	17.6		-	-	581.10	4.51	96.46	4.25	3.739	50	
434	Pt ₃₀ Cu ₇₀	16.6	600 / 7	Pt ₃₇ Cu ₆₃	17.6		-	-	674.16	5.23	111.91	4.94	3.811	24	
434	Pt ₃₀ Cu ₇₀	16.6	600 / 7	Pt ₃₇ Cu ₆₃	17.6		-	-	1270.78	6.98	210.95	6.59	3.811	24	
435	Pt ₂₅ Cu ₇₅	16.2	600 / 12	Pt ₃₅ Cu ₆₅	17.2		-	-	605.94	4.70	96.95	-	3.729	25	
436	Pt ₂₅ Cu ₇₅	16.2	600 / 12	Pt ₂₈ Cu ₇₂	14.6		-	-	605.94	4.70	96.95	5.15	3.752	24	
513	Pt ₂₅ Cu ₇₅	16.9	600 / 7	-	-		-	-	398.88	3.10	67.41	-	3.710	55	
514	Pt ₂₅ Cu ₇₅	28.6	600 / 7	-	-		-	-	192.81	1.50	55.14	-	3.713	58	
515	Pt ₂₅ Cu ₇₅	27.2	600 / 7	-	-		-	-	484.94	3.76	131.90	-	3.757	25	
516	Pt ₂₅ Cu ₇₅	14.6	600 / 7	Pt ₃₁ Cu ₆₉	13.3		-	-	799.02	6.20	116.66	6.81	3.733	17	
517	Pt ₂₅ Cu ₇₅	16.7	600 / 7	Pt ₃₂ Cu ₆₈	14.4		-	-	529.35	4.11	88.40	4.77	3.805	40	
655	Pt ₂₅ Cu ₇₅	16.2	950 / 2	Pt ₂₇ Cu ₇₃	22.4	Pt ₅₂ Cu ₄₈	18.2	25	741.31	5.75	119.87	4.15	3.710	83	1.43

656	PI30Cu70	16.8	950 / 2	-	-	PI55Cu45	18.3	-	588.84	4.57	98.63	-	3.728	63	
657	PI50Cu50	18.1	950 / 2	-	-	PI67Cu33	18.6	-	389.05	3.02	70.30	-	3.804	45	
658	PI75Cu25	18.8	950 / 2	-	-	PI84Cu16	19.0	-	194.98	1.51	36.68	-	3.869	69	
663	PI25Cu75	16.2	950 / 10	PI26Cu74	14.5	PI46Cu54	17.9	20	501.19	3.89	81.04	4.34	3.710	66	1.20
664	PI30Cu70	16.8	950 / 10	PI28Cu72	16.5	PI46Cu54	17.9	18	309.03	2.40	51.76	2.43	3.734	72	1.00
665	PI50Cu50	18.1	950 / 10	PI54Cu46	18.2	PI53Cu47	18.2	0	75.86	0.59	13.71	0.58	3.816	72	
666	PI75Cu25	18.8	950 / 10	PI71Cu29	18.7	PI72Cu28	18.7	1	77.62	0.60	14.60	0.61	3.867	93	0.29
671	PI25Cu75	16.2	900 / 2	PI28Cu72	14.9	PI60Cu40	18.4	32	707.95	5.50	114.47	5.96	3.711	41	1.27
672	PI30Cu70	16.8	900 / 2	-	-	PI60Cu40	18.4	-	630.96	4.90	105.69	-	3.720	45	1.38
673	PI50Cu50	18.1	900 / 2	-	-	PI68Cu32	18.7	-	263.03	2.04	47.53	-	3.796	45	
674	PI75Cu25	18.8	900 / 2	-	-	PI78Cu22	18.9	-	138.04	1.07	25.97	-	3.867	46	
679	PI25Cu75	16.2	900 / 10	-	-	PI58Cu42	18.4	-	588.84	4.57	95.22	-	3.703	39	1.29
680	PI30Cu70	16.8	900 / 10	-	-	PI59Cu41	18.4	-	537.03	4.17	89.95	-	3.732	41	1.33
681	PI50Cu50	18.1	900 / 10	-	-	PI64Cu36	18.5	-	251.19	1.95	45.39	-	3.791	61	
682	PI75Cu25	18.8	900 / 10	-	-	PI79Cu21	18.9	-	134.90	1.05	25.37	-	3.862	57	
687	PI25Cu75	16.2	800 / 2	PI27Cu73	14.0	PI60Cu40	18.4	33	724.44	5.62	117.14	6.50	3.701	33	1.76
688	PI30Cu70	16.8	800 / 2	-	-	PI64Cu36	18.5	-	630.96	4.90	105.69	-	3.720	37	1.62
689	PI50Cu50	18.1	800 / 2	-	-	PI71Cu29	18.7	-	360.19	2.95	68.70	-	3.806	33	
690	PI75Cu25	18.8	800 / 2	-	-	PI85Cu15	19.0	-	251.19	1.95	47.25	-	3.878	34	
695	PI25Cu75	16.2	800 / 10	PI28Cu72	15.2	PI61Cu39	18.5	33	537.03	4.17	86.84	4.43	3.689	34	1.33
696	PI30Cu70	16.8	800 / 10	-	-	PI60Cu40	18.4	-	512.86	3.98	85.90	-	3.696	34	
697	PI50Cu50	18.1	800 / 10	-	-	PI66Cu34	18.6	-	316.23	2.45	57.14	-	3.776	36	
698	PI75Cu25	18.8	800 / 10	-	-	PI78Cu22	18.9	-	144.54	1.12	27.19	-	3.859	49	
703	PI25Cu75	16.2	700 / 2	PI28Cu72	15.5	PI61Cu39	18.5	33	575.44	4.47	93.05	4.66	3.694	33	1.40
704	PI30Cu70	16.8	700 / 2	-	-	PI59Cu41	18.4	-	575.44	4.47	96.39	-	3.731	30	
705	PI50Cu50	18.1	700 / 2	-	-	PI75Cu25	18.8	-	302.00	2.34	54.57	-	3.785	25	
706	PI75Cu25	18.8	700 / 2	-	-	PI69Cu31	18.7	-	-	-	-	-	-	-	
711	PI25Cu75	16.2	700 / 10	PI29Cu71	14.6	PI73Cu27	18.8	44	676.08	5.25	109.32	5.81	3.702	30	1.33
712	PI30Cu70	16.8	700 / 10	-	-	PI66Cu34	18.6	-	588.84	4.57	98.63	-	3.725	25	1.24
713	PI50Cu50	18.1	700 / 10	-	-	PI73Cu27	18.8	-	371.54	2.88	67.14	-	3.786	25	
714	PI75Cu25	18.8	700 / 10	-	-	PI76Cu24	18.8	-	363.08	2.82	68.29	-	-	-	
719	PI25Cu75	16.2	600 / 2	PI32Cu68	15.1	PI69Cu31	18.7	37	416.87	3.24	67.41	3.47	3.700	31	1.52
720	PI30Cu70	16.8	600 / 2	-	-	PI71Cu29	18.7	-	575.44	4.47	96.39	-	3.745	24	1.52

721	PI50Cu50	18.1	600 / 2	-	-	18.8	PI77Cu23	-	354.81	2.75	64.11	-	3.812	23	
722	PI75Cu25	18.8	600 / 2	-	-	18.8	PI75Cu25	-	316.23	2.45	59.48	-	-		
727	PI25Cu75	16.2	600 / 10	PI29Cu71	14.9	18.5	PI64Cu36	35	501.19	3.89	81.04	4.22	3.699	29	1.52
728	PI30Cu70	16.8	600 / 10	-	-	18.7	PI69Cu31	-	512.86	3.98	85.90	-	3.735	24	
729	PI50Cu50	18.1	600 / 10	-	-	18.9	PI79Cu21	-	407.38	3.16	73.61	-	3.802	24	
730	PI75Cu25	18.8	600 / 10	-	-	18.8	PI75Cu25	-	346.74	2.69	65.22	-	-		
783	PI30Cu70	16.8	950 / 10	-	-	-		-	524.65	4.07	87.90	-	3.722	54	
790	PI35Cu65	17.2	950 / 10	-	-	-		-	395.67	3.07	68.06	-	3.742	52	
793	PI25Cu75	16.2	950 / 10	-	-	-		-	597.67	4.64	96.62	-	3.710	70	1.00
847	PI25Cu75	14.6	600 / 7	-	-	-		-	728.90	5.66	106.42	-	3.733	17	
848	PI25Cu75	16.2	800 / 2	PI27Cu73	16.4	-		-	524.81	4.07	84.86	-	3.694	33	1.48
970	PI25Cu75	16.2	800 / 2	PI30Cu70	16.8	18.4	PI58Cu42	28	667.25	5.18	107.89	5.00	3.696	35	
1072	PI48Cu52	21.1	N/A	PI55Cu45	18.3	18.8	PI77Cu23	22	254.72	1.98	53.75	-	3.757	28	
1073	PI61Cu39	27.0	N/A	-	-	-		-	159.32	1.24	43.02	-	3.783	60	
1074	PI63Cu37	27.1	N/A	-	-	-		-	147.77	1.15	40.05	-	3.786	62	
1077	PI25Cu75	16.2	800 / 3	PI25Cu75	16.2	18.3	PI56Cu44	31	623.77	4.84	100.86	4.84	3.701	31	1.57
1120	PI25Cu75	16.7	600 / 7	-	-	18.3	PI56Cu44	-	550.69	4.27	91.97	-	3.707	42	
1121	PI25Cu75	16.7	900 / 2	-	-	18.2	PI53Cu47	-	540.63	4.20	90.29	-	3.704	60	0.76
1202	PI25Cu75	16.2	600 / 7	-	-	-		-	683.03	5.30	-	-	-	-	1.42
1206	PI25Cu75	16.2	-	PI59Cu41	18.4	18.7	PI70Cu30	11	457.09	3.55	73.91	3.12	-	-	1.48
1866	PI15Cu85	14.2	800 / 2		14.2	18.4	PI58Cu42	43	452.59	3.51	64.16	3.51	3.701		0.95
1867	PI20Cu80	15.4	800 / 2		15.4	18.6	PI65Cu35	45	517.62	4.02	79.49	4.02	3.705		1.00
1868	PI25Cu75	16.2	800 / 2		16.2	18.3	PI56Cu44	31	579.05	4.49	93.61	4.49	3.718		1.14
1869	PI30Cu70	16.8	800 / 2		16.8	18.6	PI66Cu34	36	500.28	3.88	83.82	3.88	3.723		1.33
1870	PI35Cu65	17.2	800 / 2		17.2	18.5	PI64Cu36	29	486.20	3.77	83.64	3.77	3.732		1.33
1871	PI40Cu60	17.6	800 / 2		17.6	18.6	PI67Cu33	27	432.00	3.35	75.83	3.35	3.752		1.29
1872	PI45Cu55	17.8	800 / 2		17.8	18.6	PI66Cu34	21	275.32	2.14	49.11	2.14	3.765		1.10
1873	PI50Cu50	18.1	800 / 2		18.1	18.8	PI73Cu27	23	334.52	2.60	60.45	2.60	3.780		1.00
1874	PI15Cu85	14.2	900 / 1.2		14.2	18.3	PI57Cu43	42	430.16	3.34	60.98	3.34	3.694		0.67
1875	PI20Cu80	15.4	900 / 1.2		15.4	18.5	PI62Cu38	42	437.14	3.39	67.14	3.39	3.702		1.10
1876	PI25Cu75	16.2	900 /		16.2	18.2	PI53Cu47	28	460.30	3.57	74.41	3.57	3.709		1.05

* Samples 433 and 434 were prepared by co-precipitation. All other samples were prepared by freeze-drying.

* Samples 421 and 434 were screened at 60°C. All other samples were screened at room temperature.

Example 4 - Evaluation of Catalytic Activity of Supported Catalysts

- [0130]** The supported alloy catalysts set forth in Table P and Q, and formed according to Example 3, were subjected to electrochemical measurements to evaluate their activities. For the evaluation, the supported
- 5 catalysts were applied to a rotating disk electrode (RDE) as is commonly used in the art (see, Rotating Disk Electrode Measurements on the CO Tolerance of a High-surface Area Pt/Vulcan Carbon Fuel Cell Electrocatalyst, Schmidt et al., Journal of the Electrochemical Society (1999), 146(4), 1296-1304; and, Characterization of High Surface-Area Electrocatalysts using a Rotating Disk
- 10 Electrode Configuration, Schmidt et al., Journal of the Electrochemical Society (1998), 145(7), 2354-2358). Rotating disk electrodes are a relatively fast and simple screening tool for evaluating supported catalysts with respect to their intrinsic electrolytic activity for oxygen reduction (e.g., the cathodic reaction of a fuel cell).
- 15 **[0131]** The rotating disk electrodes were prepared by depositing an aqueous-based ink that comprises the support catalyst and a NAFION™ solution on a glassy carbon disk. The concentration of catalyst powder in the NAFION™ solution was about 1 mg/mL. The NAFION™ solution comprised the perfluorinated ion-exchange resin, lower aliphatic alcohols and water, wherein
- 20 the concentration of resin was about 5 percent by weight. The NAFION™ solution is commercially available from ALDRICH as product number 27,470-4. The glassy carbon electrodes were 5 mm in diameter and were polished to a mirror finish. Glassy carbon electrodes are commercially available, for example, from Pine Instrument Company of Grove City, Pennsylvania. For each
- 25 electrode, an aliquot of 10 μ L the catalyst suspension was deposited on to the glass carbon disk and allowed to dry at a temperature between about 60 and 70°C. The resulting layer of NAFION™ and catalyst was less than about 0.2 μ m thick. This method produced slightly different platinum loadings for each electrode made with a particular suspension, but the variation was determined to
- 30 be less than about 10 percent by weight.

[0132] After being dried, each rotating disk electrode was immersed into an electrochemical cell comprising an aqueous 0.5 M H₂SO₄ electrolyte solution maintained at room temperature. Before performing any measurements, the electrochemical cell was purged of oxygen by bubbling argon through the electrolyte for about 20 minutes. All measurements were taken while rotating the electrode at about 2000 rpm, and the measured current densities were normalized either to the glassy carbon substrate area or to the platinum loading on the electrode. Two groups of tests were performed to screen the activity of the supported electrocatalysts. The first group of tests comprised cyclic voltammetric measurements while purging the electrolyte with argon.

Specifically, the first group comprised:

- a. two consecutive potential sweeps starting from OCP to about +0.35V then to about -0.65V and back to OCP at a rate of about 50 mV/s;
- b. two hundred consecutive potential sweeps starting from OCP to about +0.35V then to about -0.65V and back to OCP at a rate of about 200 mV/s; and
- c. two consecutive potential sweeps starting from OCP to about +0.35V then to about -0.65V and back to OCP at a rate of about 50 mV/s.

The second test comprised purging with oxygen for about 15 minutes followed by a potential sweep test for oxygen reduction while continuing to purge the electrolyte with oxygen. Specifically, potential sweeps from about -0.45 V to +0.35 V were performed at a rate of about -5 mV/s to evaluate the initial activity of the catalyst as a function of potential and to create a geometric current density plot. The catalysts were evaluated by comparing the diffusion corrected activity at 0.15 V. All the foregoing test voltages are with reference to a mercury/mercury sulfate electrode. Also, it is to be noted that the oxygen reduction measurements for a glassy carbon RDE without a catalyst did not show any appreciable activity within the potential window.

[0133] The above-described supported catalyst compositions were evaluated in accordance with the above-described method and the results are set forth in Tables P and Q. It is to be noted from the results presented therein

that substantially all of the carbon supported catalyst compositions exhibited an oxygen reduction activity which exceeded, for example, the carbon supported platinum standard (see, e.g., samples HFC 363, 369-374, 382-84, 387, 389 and 390 in Table P and samples HFC 434, 516, 687, 711 and 847 in Table Q).

5 **[0134]** The results of the evaluation indicate, among other things, that a supported catalyst of the present invention may be produced using different method conditions (e.g., temperature and/or duration). It is to be noted, however, that it may take numerous iterations to develop a set of parameters for producing a particular catalyst composition. Also evidenced by the data is that
10 activity may be adjusted by changes in the method conditions.

[0135] Further, without being held to a particular theory, it is presently believed that differences in activity for similar catalyst compositions may be due to several factors, such as homogeneity (e.g., an alloy, as defined herein, may have regions in which the constituent atoms show a presence or lack of order,
15 i.e., regions of solid solution within an ordered lattice, or some type of superstructure), changes in the lattice parameter due to changes in the average size of component atoms, changes in particle size, and changes in crystallographic structure/symmetry. The ramifications of synthesis, structure and symmetry changes are often difficult to predict. For example, while it may
20 be expected that within the Pt-Cu system the two metals will be fully miscible, the possibility exists that ordering may occur between the two metals at the atomic level. The possibility further exists that as the relative ratio of copper to platinum changes, a solid solution may crystallize (e.g., $Pt_{1-x}Cu_x$), and out of this solid solution an ordered phase may gradually crystallize (e.g., $Pt_{50}Cu_{50}$), only to
25 return to a solid solution (disordered alloy), and again back to an ordered phase (e.g., $Pt_{25}Cu_{75}$).

[0136] Symmetry changes (e.g., those associated with the changes from a cubic face centered structure to another structure type, such as a tetragonal or hexagonal structure for example) may result in significant changes in the X-ray
30 diffraction pattern. These changes may also be accompanied by more subtle changes in lattice parameters that may be indicative of the resulting changes in the size of the respective metal constituents. For example, the 12-coordinate metallic radii of platinum and copper are 1.387 Å and 1.278 Å, respectively, and

as one metal is substituted for another, the average metal radius and, consequently, the observed lattice parameter, may be expected to shrink or expand accordingly. The average radius may be used as an indicator of lattice changes as a function of stoichiometry, or alternatively, as an indicator of stoichiometry based on observed lattice parameters. It should be noted, however, that while average radii may be useful as a general rule, experimental results should be expected to conform only in a general manner because local ordering, significant size disparity between atoms, significant changes in symmetry, and/or other factors may produce values that are inconsistent with expectations. Occasionally, however, the use of alternative metallic radii may be informative. One such alternative radius concept approximates metal radii using known crystallographically ordered Pt-based alloys, such as PtCu (wherein cubic symmetry is maintained), instead of pure metals. (See, e.g., Pearson's Handbook, P. Villars, ed., ASM International, 1997.) In this case, the same close-packed geometric arguments are relevant, with the exception that the lattice parameter of the ordered metal alloy is used in conjunction with the accepted 12-coordinate metallic radius of platinum, *supra*. Using these concepts, it is believed that the effective radius of copper is about 1.284 Å.

[0137] An interpretation of XRD analyses for a few of the foregoing supported catalysts is set forth below. It is to be noted, however, that interpretation of XRD analyses can be subjective, and therefore, the following conclusions are not intended to be limiting.

[0138] At least a portion of the catalyst powders listed in Tables P and Q were analyzed to determine both the lattice parameter, assuming a face-centered cubic lattice, and the observed particle size (i.e., the size of the metal-containing deposits on the supports). The peak positions were corrected using silicon powder (SRM 640c). The average particle sizes of the catalyst deposits, not of any copper or copper-rich impurity phases, were determined using the Scherrer formula. The term "particle size" as used herein with respect to the size of metal deposits on the supports shall be interpreted as the average particle size. The supported platinum powder used to prepare, with few exceptions (e.g., sample HFC 374-381), the catalyst powders described herein (i.e., the standard supported platinum powder) had a particle size of

approximately 19 Å. The HFC 374-381 catalysts were prepared with two alternative supported platinum powders. The HFC 374, 375, 378 and 379 were prepared with a first alternative supported platinum powder that consisted of carbon supports as described above with platinum metal deposits having a particle size that is smaller than 19 Å. Specifically, the first alternative powder has a loading of between about 16 and about 18 weight percent, and a particle size of about 12 and about 19 Å. The second alternative powder has a platinum loading of between about 30 and about 35 weight percent.

[0139] All of the catalysts of Table P and Q displayed XRD patterns of a face-centered cubic ("fcc") material, or a fcc-based material. Certain materials displayed slight indications of ordering (see description of the different catalysts below). In general, the observed lattice parameters of the catalyst compositions in Tables P and Q agreed with what was expected for the particular target catalyst compositions. However, in some circumstances, the lattice parameters were larger than what was anticipated, and based on the XRD profile (e.g., the presence of additional peaks or peak shape irregularities) it is believed that this discrepancy is due, at least in part, to the presence of incompletely reacted, or alloyed, copper or copper-rich impurities. For example, referring now to Figure 5, the general background pattern is due to the presence of carbon; peaks A, B, and C are that of a platinum-copper alloy deposits and peaks X, Y, and Z are that of copper and/or copper-rich impurity deposits. The narrower aspect of the copper/copper-rich impurity peaks is due to the fact that the impurity deposits are larger in size than the platinum-copper alloy deposits. Because of the presence of copper or copper-rich impurities, the amount of platinum in the alloy deposits is actually greater than the target composition and this results in a larger observed lattice parameter. Additionally, the results generally indicate that as the copper content in the target stoichiometry increases there is greater tendency to have more unreacted, or unalloyed, copper or copper-rich impurities for syntheses at a given temperature/time.

[0140] The observed lattice parameters of the $\text{Pt}_{16}\text{Cu}_{84}$ catalysts (HFC 360 and 367) are consistent with the amount of copper impurities (i.e., although the global stoichiometry of the supported catalyst may be $\text{Pt}_{16}\text{Cu}_{84}$, the presence of the copper impurities results in an empirical stoichiometry of $\text{Pt}_{16+x}\text{Cu}_{84-x}$ and a

concomitant increase in the observed lattice parameter). Specifically, the lattice parameters of HFC 360 and 367 are about 3.705 Å and about 3.702 Å , respectively, and the relative performance of HFC 367 is about 18.5% greater than HFC 360. Additionally, the differences in heat treatments resulted in
5 differences in particle sizes; the observed lattice parameters of the Pt₂₀Cu₈₀ catalysts (HFC 361 and 368) are similarly consistent with the amount of copper impurities.

[0141] The observed lattice parameters of the Pt₂₅Cu₇₅ catalysts in Table P (HFC 344, 362, 369, 374, 376, 378, 380, 382 and 387) varied according to the
10 starting supported platinum powder that was used. In general, the alloys prepared from the alternative supported platinum powders (HFC 374, 376, 378 and 380) had larger lattice parameters, and more crystalline copper or copper-rich impurities. Accordingly, the electrochemical performance of these materials suffered compared to the materials prepared using the standard supported
15 platinum powder. The observed lattice parameters for alloys prepared using the standard supported platinum powder are consistent with each other and the alloy stoichiometry as measured by EDS. At this time, it is not fully understood why the catalysts produced by the alternative powders were less reacted than those produced with the standard powder. However, it is believed that more
20 complete alloying may be achieved through routine experimentation to determine the optimum values of one or more method parameters, such as alloying temperature and/or duration. Upon determining the optimum values, it is possible that the alternative supported platinum powders, especially the powder having platinum particles of a size less than the standard powder, will
25 result alloy particles that yield greater electrochemical performance due, at least in part, to the smaller particle size.

[0142] The observed lattice parameters of the Pt_{27.5}Cu_{72.5} catalysts (HFC383 and 388) are generally consistent with the stoichiometry as measured by EDS. The differences in particle sizes are also consistent with the synthesis
30 temperatures and seem to contribute to electrochemical performance (i.e., lower synthesis temperatures tend to produce smaller particles that tend to result in greater electrochemical activity than larger particles of the same composition).

[0143] The observed lattice parameters of the $\text{Pt}_{30}\text{Cu}_{70}$ catalysts (HFC 345, 363, 370, 375, 377, 379, 381, 384 and 389) vary according to the starting material used. In general, the alloys prepared from the alternative supported platinum powders (HFC 375, 377, 379 and 381) had larger lattice parameters
5 and more copper or copper-rich impurities. Accordingly, the electrochemical performance of these materials suffered compared to the materials prepared using the standard supported platinum powder. The observed lattice parameters for alloys prepared using the standard supported platinum powder are consistent with each other and the alloy stoichiometry as measured by EDS.
10 Among the alloys prepared using the standard supported platinum powder, those with more copper or copper-rich impurities tend to under-perform electrochemically.

[0144] The observed lattice parameters of the $\text{Pt}_{32.5}\text{Cu}_{67.5}$ catalysts (HFC 385 and 390) are larger than expected. Specifically, the observed parameters
15 for HFC 854 and 390 are 3.760 and 3.764, respectively, whereas the calculated lattice parameter is 3.725. The observed particle sizes are consistent with the synthesis temperature (i.e., higher synthesis temperatures tend to produce larger the particles).

[0145] The observed lattice parameters of the $\text{Pt}_{35}\text{Cu}_{65}$ catalysts (HFC
20 287, 290, 364, 371, 386 and 391) are generally consistent with the observed copper or copper-rich impurities. The particle sizes increased with increasing synthesis temperatures. The observed electrochemical activity of the 900 °C material was less than that for the 700 °C material. The electrochemical activity of the 700 °C materials is considered to be consistent with stoichiometry. It is
25 believed that the relatively low electrochemical performance of HFC 386 is due to incomplete alloying at the relatively low temperature of 600 °C.

[0146] The $\text{Pt}_{40}\text{Cu}_{60}$ catalysts (HFC 346, 365 and 372) seem to be consistent with the general rule that increasing synthesis temperature tend to result in increasing particle size and decreasing electrochemical activity. The
30 lattice parameter of HFC 346 is largest because it had the largest amount of copper and/or copper-rich impurities. This is believed to be a reason why it had a lower activity than the HFC 365 catalyst, which was also prepared at 700 °C.

[0147] The observed lattice parameter of the Pt₄₅Cu₅₅ catalyst (HFC 347) is larger than expected for the stoichiometry because of copper and/or copper-rich impurities as previously discussed. The observed particle size is consistent with the synthesis temperature.

5 **[0148]** In view of the foregoing, for a particular catalyst composition, a determination of the optimum conditions is preferred to produce the highest activity for that particular composition. In fact, for certain catalyst compositions, different structural characteristics may define what exactly is described as a good catalyst. These characteristics may include differences in the composition
10 (as viewed by lattice parameter), crystallinity, crystallographic ordering and/or particle size. These characteristics are not necessarily predictable and may depend on a complex interplay between starting materials, synthesis method, synthesis temperature and composition. For example, the starting materials used to synthesize the catalyst alloy may play a role in the activity of the
15 synthesized catalyst alloy. Specifically, using something other than a metal nitrate salt solution to supply the metal atoms may result in different activities. Additionally, alternative Pt sources may be employed. Freeze-drying and heat treatment parameters such as atmosphere, time, temperature, etc. may also need to be optimized. This optimization may be compositionally dependent.
20 Additionally, this optimization may involve balancing competing phenomena. For example, increasing the heat treatment temperature is generally known to improve the reduction of a metal salt to a metal, which typically increases activity; however, this also tends to increase the size of the catalyst alloy particle and decrease surface area, which decreases electrocatalytic activity.

25 Example 5 - Washing of Catalyst Composition Precursor

[0149] Additional Pt-Cu catalyst compositions (see Tables R1 and R2, *infra*) were prepared and evaluated for catalytic activity, generally in accordance with the approaches outlined in Examples 3 and 4, respectively (and as further detailed in Tables R1 and R2). However, after initial preparation and prior to
30 testing, these compositions were subjected to one of various washing procedures (as further detailed in Tables R1 and R2, *infra*), in order to dissolve

or remove a portion of the copper present therein.

[0150] To illustrate one preferred approach, 100 mg of a catalyst composition precursor (e.g., HFC 1077, $\text{Pt}_{25}\text{Cu}_{75}$), was placed into a 20 ml glass vial followed by the slow addition of 15 ml of a 1 M HClO_4 acid solution (added 5 slowly, over a 5 to 10 second period of time, in order to allow sufficient time for the acid to wet the powder). This mixture was placed on a hot plate that had been previously calibrated to raise the temperature of the mixture to 90-95°C (the vial in which the mixture had been placed being capped, but not tightly, so that any boiling which occurred took place without a build-up of pressure 10 therein).

[0151] After 1 hour under these conditions, the mixture was filtered through filter paper, the filtrate having a pale blue color indicating the presence of Cu ions therein. The filtered cake was washed repeatedly with a large excess of water.

15 **[0152]** Following this initial, single wash cycle, the isolated filter cake was placed into a new vial with another 15 ml of 1 M HClO_4 acid solution. After sufficient stirring to break apart the filter cake, the mixture was returned to the hot plate at 90-95°C for 1 hour. The mixture was then filtered and washed with water. The resulting cake was dried at 90°C for 48 hours.

Table R1

Powder Number	Powder Precursor Number	Target Catalyst Comp. before washing	Precursor Max Alloying Temp. for a duration (°C/hrs)	Acid identity	Acid Molarity	Acid temp. (°C)	Wash time (min)	# of washes	Wash technique	Wash gas	Notes	Actual Catalyst Comp. after washing	Actual Loading after wash (from EDS) (wt%)
566	435	Pt25Cu75	600/12	H2SO4	0.5	25	30	1	Soak	ambient		Pt55Cu45	18.27
608	435	Pt25Cu75	600/12	CF3SO3H	1	25	30	1	Soak	ambient		Pt62Cu38	18.49
645	435	Pt25Cu75	600/12	H2SO4	0.5	25	30	1	Soak	O2		Pt50Cu50	18.07
646	435	Pt25Cu75	600/12	H2SO4	0.5	25	30	1	Soak	Ar		Pt48Cu52	17.98
873	848	Pt25Cu75	800/2	H2SO4	0.5	25	12	1	Centrifuge	ambient	a	Pt39Cu61	17.50
874	848	Pt25Cu75	800/2	H2SO4	0.05	25	12	1	Centrifuge	ambient	a	Pt36Cu64	17.28
875	848	Pt25Cu75	800/2	CF3SO3H	1	25	12	1	Centrifuge	ambient	a	Pt36Cu64	17.25
876	848	Pt25Cu75	800/2	CF3SO3H	0.1	25	12	1	Centrifuge	ambient	a	Pt33Cu67	17.08
877	848	Pt25Cu75	800/2	H2SO4	0.5	25	7	1	Centrifuge	ambient	a	Pt31Cu69	16.81
878	848	Pt25Cu75	800/2	H2SO4	0.05	25	7	1	Centrifuge	ambient	a	Pt31Cu69	16.82
879	848	Pt25Cu75	800/2	CF3SO3H	1	25	7	1	Centrifuge	ambient	a	Pt34Cu66	17.10
880	848	Pt25Cu75	800/2	CF3SO3H	0.1	25	7	1	Centrifuge	ambient	a	Pt30Cu70	16.74
881	848	Pt25Cu75	800/2	H2SO4	0.5	25	4	1	Centrifuge	ambient	a	Pt28Cu72	16.49
882	848	Pt25Cu75	800/2	H2SO4	0.05	25	4	1	Centrifuge	ambient	a	Pt27Cu73	16.40
883	848	Pt25Cu75	800/2	CF3SO3H	1	25	4	1	Centrifuge	ambient	a	Pt24Cu76	15.99
884	848	Pt25Cu75	800/2	CF3SO3H	0.1	25	4	1	Centrifuge	ambient	a	Pt24Cu76	16.03
885	848	Pt25Cu75	800/2	HClO4	1	25	12	1	Centrifuge	ambient	a	Pt36Cu64	17.30
886	848	Pt25Cu75	800/2	HClO4	0.1	25	12	1	Centrifuge	ambient	a	Pt29Cu71	16.65
887	848	Pt25Cu75	800/2	HClO4	1	25	7	1	Centrifuge	ambient	a	Pt37Cu63	17.34
888	848	Pt25Cu75	800/2	HClO4	0.1	25	7	1	Centrifuge	ambient	a	Pt35Cu65	17.19
889	848	Pt25Cu75	800/2	HClO4	1	25	4	1	Centrifuge	ambient	a	Pt42Cu58	17.66
890	848	Pt25Cu75	800/2	HClO4	0.1	25	4	1	Centrifuge	ambient	a	Pt33Cu67	17.02
892	848	Pt25Cu75	800/2	H2SO4	0.5	25	12	1	Centrifuge/ Sonification	ambient	b	Pt52Cu48	18.15
893	848	Pt25Cu75	800/2	H2SO4	0.05	25	12	1	Centrifuge/ Sonification	ambient	b	Pt45Cu55	17.85
894	848	Pt25Cu75	800/2	CF3SO3H	1	25	12	1	Centrifuge/ Sonification	ambient	b	Pt48Cu52	17.97

895	848	Pt25Cu75	800/2	CF3SO3H	0.1	25	12	1	Centrifuge/ Sonification	ambient	b	Pt48Cu52	17.99
912	848	Pt25Cu75	800/2	H2SO4	0.05	25	5	1	Sonification	ambient		Pt38Cu62	17.44
913	848	Pt25Cu75	800/2	Nafion	-	25	-	-	Filtration	ambient			
938	848	Pt25Cu75	800/2	HClO4	1	25	5	1	Sonification	ambient		Pt46Cu54	17.89
939	848	Pt25Cu75	800/2	HClO4	1	25	5	1	Sonification	Ar		Pt44Cu56	17.79
940	848	Pt25Cu75	800/2	Nafion	-	-	-	-	Filtration	ambient	c	Pt48Cu52	17.98
941	695	Pt25Cu75	800/10	Nafion	-	-	-	-	Centrifuge	ambient		Pt40Cu60	17.56
942	435	Pt25Cu75	600/12	H2SO4	0.5	25	30	1	Soak	ambient		Pt52Cu48	18.14
943	435	Pt25Cu75	600/12	H2SO4	0.5	25	30	1	Soak	O2		Pt51Cu49	18.11
968	848	Pt25Cu75	800/2	Nafion	-	25	-	1	Centrifuge	ambient		Pt35Cu65	17.17
969	848	Pt25Cu75	800/2	H2SO4	0.5	25	20	1	Soak	ambient		Pt35Cu65	17.19
995	848	Pt25Cu75	800/2	H2SO4	0.5	25	-	1	Electro-chemical	ambient	d	Pt53Cu47	18.19
996	970	Pt25Cu75	800/2	H2SO4	0.5	25	20	1	Sonification	ambient		Pt49Cu51	18.01
997	970	Pt25Cu75	800/2	H2SO4	0.5	90	20	1	Soak	ambient		Pt46Cu54	17.87
998	970	Pt25Cu75	800/2	H2SO4	0.5	25	60	1	Soak	ambient		Pt43Cu57	17.74
999	970	Pt25Cu75	800/2	H2SO4	0.5	90	60	1	Soak	ambient		Pt51Cu49	18.12
1000	970	Pt25Cu75	800/2	H2SO4	5	25	20	1	Soak	ambient		Pt44Cu56	17.79
1001	970	Pt25Cu75	800/2	H2SO4	5	90	20	1	Soak	ambient		Pt48Cu52	18.00
1002	970	Pt25Cu75	800/2	H2SO4	5	25	60	1	Soak	ambient		Pt39Cu61	17.49
1003	970	Pt25Cu75	800/2	H2SO4	5	90	60	1	Soak	ambient		Pt51Cu49	18.10
1012	970	Pt25Cu75	800/2	H2SO4	0.5	25	10	2	Soak	ambient	e	Pt59Cu41	18.41
1013	970	Pt25Cu75	800/2	H2SO4	0.5	25	60	2	Soak	ambient		Pt56Cu44	18.30
1014	970	Pt25Cu75	800/2	H2SO4	0.5	25	60	2	Soak	ambient		Pt61Cu39	18.47
1015	970	Pt25Cu75	800/2	H2SO4	5	25	10	2	Soak	ambient		Pt49Cu51	18.04
1016	970	Pt25Cu75	800/2	H2SO4	5	25	60	2	Soak	ambient		Pt55Cu45	18.25
1029	970	Pt25Cu75	800/2	H2SO4	0.5	25	60	3	Soak	ambient		Pt65Cu35	18.59
1030	970	Pt25Cu75	800/2	H2SO4	0.5	25	60	4	Soak	ambient		Pt67Cu33	18.62
1031	970	Pt25Cu75	800/2	H2SO4	5	25	60	3	Soak	ambient		Pt59Cu41	18.41
1032	970	Pt25Cu75	800/2	H2SO4	5	25	60	4	Soak	ambient		Pt64Cu36	18.55
1057	970	Pt25Cu75	800/2	HNO3	1	25	10	1	Soak	ambient		Pt53Cu47	18.21
1058	970	Pt25Cu75	800/2	HNO3	1	25	60	1	Soak	ambient		Pt47Cu53	17.95
1059	970	Pt25Cu75	800/2	HNO3	5	25	10	1	Soak	ambient		Pt51Cu49	18.12
1060	970	Pt25Cu75	800/2	HNO3	5	25	60	1	Soak	ambient		Pt59Cu41	18.40
1061	970	Pt25Cu75	800/2	HClO4	1	90	60	2	Soak	ambient		Pt57Cu43	18.32

1062	970	Pt25Cu75	800/2	H2SO4	0.5	90	60	2	Soak	ambient	Pt59Cu41	18.41
1063	970	Pt25Cu75	800/2	HClO4	1	90	60	2	Soak	ambient	Pt54Cu46	18.21
1064	970	Pt25Cu75	800/2	H2SO4	0.5	90	60	2	Soak	ambient		
1065	970	Pt25Cu75	800/2	HClO4	1	90	60	2	Soak	ambient	Pt54Cu46	18.21
1066	970	Pt25Cu75	800/2	H2SO4	0.5	90	60	2	Soak	ambient		
1078	1077	Pt25Cu75	800/3	H2SO4	5	25	60	2	Soak	ambient	Pt49Cu51	18.03
1089	1077	Pt25Cu75	800/3	HClO4	1	90	60	2	Soak	ambient	Pt59Cu41	18.40
1183	848	Pt25Cu75	800/2	HClO4	1	25	60	2	Soak	ambient	Pt59Cu41	18.40
1184	848	Pt25Cu75	800/2	HClO4	1	25	60	2	Soak	ambient	Pt66Cu34	18.60
1185	848	Pt25Cu75	800/2	HClO4	1	90	60	1	Soak	ambient	Pt47Cu53	17.94
1882	1866	Pt15Cu85	800/2	HClO4	1	90	60	2	Soak	ambient	Pt53Cu47	18.19
1883	1867	Pt20Cu80	800/2	HClO4	1	90	60	2	Soak	ambient	Pt55Cu45	18.25
1884	1868	Pt25Cu75	800/2	HClO4	1	90	60	2	Soak	ambient	Pt54Cu46	18.23
1885	1869	Pt30Cu70	800/2	HClO4	1	90	60	2	Soak	ambient	Pt64Cu36	18.55
1886	1870	Pt35Cu65	800/2	HClO4	1	90	60	2	Soak	ambient	Pt62Cu38	18.47
1887	1871	Pt40Cu60	800/2	HClO4	1	90	60	2	Soak	ambient	Pt64Cu36	18.55
1888	1872	Pt45Cu55	800/2	HClO4	1	90	60	2	Soak	ambient	Pt68Cu32	18.63
1889	1873	Pt50Cu50	800/2	HClO4	1	90	60	2	Soak	ambient	Pt72Cu28	18.74
1890	1874	Pt15Cu85	900/1.2	HClO4	1	90	60	2	Soak	ambient	Pt45Cu55	17.84
1891	1875	Pt20Cu80	900/1.2	HClO4	1	90	60	2	Soak	ambient	Pt57Cu43	18.34
1892	1876	Pt25Cu75	900/1.2	HClO4	1	90	60	2	Soak	ambient	Pt56Cu44	18.30
1893	1877	Pt30Cu70	900/1.2	HClO4	1	90	60	2	Soak	ambient	Pt62Cu38	18.49
1894	1878	Pt35Cu65	900/1.2	HClO4	1	90	60	2	Soak	ambient	Pt65Cu35	18.57
1895	1879	Pt40Cu60	900/1.2	HClO4	1	90	60	2	Soak	ambient	Pt69Cu31	18.68
1896	1880	Pt45Cu55	900/1.2	HClO4	1	90	60	2	Soak	ambient	Pt69Cu31	18.68
1897	1881	Pt50Cu50	900/1.2	HClO4	1	90	60	2	Soak	ambient	Pt70Cu30	18.70
1902	1853	Pt25Cu75	800/2	HClO4	1	90	60	2	Soak	ambient		
1903	1853	Pt25Cu75	800/2	poly phosphoric	105%	200	240	1	Soak	N2	Pt58Cu42	18.37

NOTES: a = sample isolated using a 2 minute centrifuge cycle.

b = sample washed using a 1 minute sonication cycle and isolated using a 5 minute centrifuge cycle.

c = sample isolated by filtration and rinsed with propanol.

d = electrochemical wash of the powder was performed.

e = first wash at 90°C, and second at 25°C.

f = first wash performed for 60 minutes, and the second for 20 minutes.

Table R2

Powder Number	Powder Precursor Number	Actual Catalyst Comp. after screening	Pt Loading after screening (wt%)	Pt change in %	Pt Mass Activity at +0.15 V MMS (mA/mg Pt)	Relative performance at +0.15 V MMS	Catalyst Mass Activity at +0.15 V MMS (mA/mg)	Actual Relative performance at +0.15 V MMS data	Lattice parameter (Å), uncorrected	Approx. particle size (Å)	electrochemical surface area [cm ²]
566	435		-	-	401.26	3.11	64.20	2.76	3.761	-	
608	435		-	-	332.12	2.58	62.44	2.25	3.763	-	
645	435	Pt66Cu34	18.6	16	332.32	2.58	66.46	2.31	3.808	22	1.11
646	435	Pt52Cu48	18.2	4	426.70	3.31	85.77	2.98	3.755	26	1.14
873	848	Pt67Cu33	18.6	28	420.51	3.26	67.99	3.02	3.751	27	1.29
874	848	Pt71Cu29	18.7	35	447.93	3.48	72.42	3.25	3.754	-	
875	848	Pt58Cu42	18.4	22	451.85	3.51	73.05	3.29	3.750	28	1.33
876	848	Pt61Cu39	18.5	28	447.57	3.47	72.36	3.29	3.750	-	
877	848	Pt60Cu40	18.4	29	437.60	3.40	70.75	3.27	3.758	26	1.29
878	848	Pt57Cu43	18.3	26	511.03	3.97	82.62	3.81	3.740	24	
879	848	Pt56Cu44	18.3	22	473.98	3.68	76.63	3.48	3.745	25	1.29
880	848	Pt59Cu41	18.4	29	461.00	3.58	74.53	3.46	3.745	26	1.33
881	848	Pt61Cu39	18.5	33	553.44	4.30	89.48	4.21	3.740	26	1.52
882	848	Pt57Cu43	18.3	30	596.62	4.63	96.46	4.57	3.740	26	1.48
883	848	Pt66Cu34	18.6	42	551.30	4.28	89.13	4.33	3.745	25	1.43
884	848	Pt62Cu38	18.5	38	511.56	3.97	82.71	4.01	3.750	26	1.48
885	848	Pt62Cu38	18.5	26	461.95	3.59	74.69	3.35	3.754	26	1.48
886	848	Pt64Cu36	18.5	35	422.51	3.28	68.31	3.18	3.750	25	0.86
887	848	Pt64Cu36	18.5	27	502.39	3.90	81.22	3.64	3.784	25	1.00
888	848	Pt60Cu40	18.4	25	502.17	3.90	81.19	3.67	3.750	28	1.67
889	848	Pt60Cu40	18.4	18	571.88	4.44	92.46	4.06	3.741	26	1.62

890	848	Pt61Cu39	18.5	28	553.76	4.30	89.53	4.08	3.732	27	1.52
892	848	Pt62Cu38	18.5	10	261.76	2.03	42.32	1.81	3.775	-	
893	848	Pt72Cu28	18.7	27	408.67	3.17	66.07	2.87	3.774	-	
894	848	Pt72Cu28	18.7	24	331.25	2.57	53.55	2.31	3.784	24	1.38
895	848	Pt71Cu29	18.7	23	407.36	3.16	65.86	2.84	3.769	-	
912	848	Pt61Cu39	18.5	23	630.87	4.90	102.00	4.54	3.726	27	
913	848				-	-	-	-	3.706	-	
938	848				366.32	2.84	59.23	2.57	3.750	28	1.43
939	848	Pt73Cu27	18.8	29	274.79	2.13	44.43	1.94	3.779	22	0.52
940	848				86.69	0.67	14.02	0.61	3.699	31	0.43
941	695	Pt55Cu45	18.3	15	798.18	6.20	129.05	5.70	-	-	
942	435	Pt67Cu33	18.6	15	519.02	4.03	83.91	3.59	-	-	
943	435	Pt67Cu33	18.6	16	583.92	4.53	94.41	4.05	-	-	2.38
968	848				-	-	-	-	3.688	-	
969	848	Pt66Cu34	18.6	31	679.60	5.28	109.87	4.96	3.712	31	
995	848	Pt72Cu28	18.7	19	459.18	3.56	74.24	3.17	3.754	-	
996	970	Pt67Cu33	18.6	18	465.04	3.61	75.19	3.24	3.740	-	
997	970	Pt60Cu40	18.4	14	461.67	3.58	74.64	3.24	3.735	31	1.81
998	970	Pt61Cu39	18.5	18	494.69	3.84	79.98	3.50	3.728	31	
999	970	Pt62Cu38	18.5	11	408.79	3.17	66.09	2.83	3.736	25	1.52
1000	970	Pt61Cu39	18.5	17	410.12	3.18	66.31	2.89	3.731	29	1.48
1001	970	Pt66Cu34	18.6	18	430.80	3.34	69.65	3.00	3.735	-	
1002	970	Pt61Cu39	18.5	22	538.79	4.18	87.11	3.87	3.708	34	
1003	970	Pt65Cu35	18.6	14	615.19	4.78	99.46	4.27	3.732	29	
1012	970	Pt70Cu30	18.7	11	-	-	-	-	-	-	
1013	970	Pt67Cu33	18.6	11	555.95	4.32	89.88	3.81	3.763	26	2.00
1014	970	Pt64Cu36	18.5	3	412.62	3.20	66.71	2.80	3.763	25	1.90
1015	970	Pt60Cu40	18.4	11	420.39	3.26	67.97	2.93	3.742	28	1.62
1016	970	Pt62Cu38	18.5	7	497.91	3.87	80.50	3.42	3.748	29	1.52
1029	970	Pt70Cu30	18.7	5	395.05	3.07	63.87	2.67	3.777	23	2.10
1030	970	Pt76Cu24	18.8	9	426.44	3.31	68.94	2.87	3.787	26	2.14
1031	970	Pt72Cu28	18.7	13	460.98	3.58	74.53	3.14	3.782	-	
1032	970	Pt72Cu28	18.7	8	378.25	2.94	61.15	2.56	3.782	-	
1057	970	Pt62Cu38	18.5	9	495.55	3.85	80.12	3.42	3.758	29	2.00
1058	970	Pt70Cu30	18.7	23	460.40	3.57	74.43	3.22	3.758	27	1.90
1059	970	Pt75Cu25	18.8	24	465.03	3.61	75.18	3.22	3.767	25	1.95

1060	970	Pt71Cu29	18.7	12	436.28	3.39	70.54	2.98	3.792	23	1.71
1061	970	Pt54Cu46	18.2	-3	281.83	2.19	45.56	1.93	3.744	-	
1062	970	Pt65Cu35	18.6	6	263.02	2.04	42.52	1.79	3.782	-	
1063	970	Pt54Cu46	18.2	0	-	-	-	-	-	-	
1064	970				-	-	-	-	-	-	
1065	970	Pt54Cu46	18.2	0	398.09	3.09	64.36	2.74	-	-	
1066	970				370.67	2.88	59.93	N/A	-	-	
1078	1077	Pt61Cu39	18.5	12	489.52	3.80	79.14	3.41	3.738	28	1.71
1089	1077	Pt65Cu35	18.6	6	463.75	3.60	74.98	3.16	3.767	-	1.48
1183	848	Pt68Cu32	18.7	9	395.18	3.07	63.89	2.70	3.782	24	1.90
1184	848	Pt71Cu29	18.7	5	422.23	3.28	68.26	2.85	3.777	25	1.62
1185	848	Pt58Cu42	18.4	11	550.35	4.27	88.98	3.85	3.748	30	1.43
1882	1866	Pt59Cu41	18.4	6	471.28	3.66	66.81	2.85	3.730		1.19
1883	1867	Pt60Cu40	18.4	5	364.85	2.83	56.03	2.39	3.738		1.14
1884	1868	Pt64Cu36	18.5	10	377.28	2.93	60.99	2.60	3.742		1.33
1885	1869	Pt68Cu32	18.7	4	304.12	2.36	50.95	2.14	3.766		1.24
1886	1870	Pt63Cu37	18.5	1	353.82	2.75	60.86	2.55	3.778		1.00
1887	1871	Pt66Cu34	18.6	2	228.31	1.77	40.08	1.68	3.801		1.00
1888	1872	Pt73Cu27	18.8	5	225.24	1.75	40.17	1.67	3.791		0.95
1889	1873	Pt74Cu26	18.8	2	277.87	2.16	50.21	2.08	3.813		0.95
1890	1874	Pt54Cu46	18.2	9	398.66	3.09	56.51	2.46	3.726		1.24
1891	1875	Pt62Cu38	18.5	5	312.99	2.43	48.07	2.04	3.747		1.14
1892	1876	Pt59Cu41	18.4	3	306.78	2.38	49.60	2.10	3.749		1.10
1893	1877	Pt67Cu33	18.6	5	275.38	2.14	46.14	1.94	3.771		1.05
1894	1878	Pt64Cu36	18.5	-1	332.69	2.58	57.23	2.39	3.778		1.00
1895	1879	Pt70Cu30	18.7	1	229.00	1.78	40.20	1.67	3.797		0.90
1896	1880	Pt73Cu27	18.8	4	186.90	1.45	33.34	1.38	3.811		0.86
1897	1881	Pt79Cu21	18.9	9	206.73	1.60	37.36	1.54	3.817		0.90
1902	1853				421.25	3.27	68.10				
1903	1853	Pt67Cu33	18.6	9	414.70	3.22	67.04	2.83			

[0153] Generally speaking, it is to be noted from the data presented above that, surprisingly, it appears the washing procedure described herein does not necessarily always increase the surface area of the catalyst compositions. This relationship is independent of the annealing temperature of
5 the catalyst. Without being held to any particular theory, it is believed that this may be due to the fact that a more traditional skeleton catalyst, such as that reported for example in U.S. Patent No. 5,876,687, is not being formed here, or is not being formed in the same manner, perhaps due at least in part to the presence of oxygen here. This theory is supported by the relationship of
10 measured composition after washing and measured lattice parameters. Particle size appears to decrease upon washing, however, perhaps indicative of some collapse of the skeleton framework due to the presence of oxygen.

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[0154] It is to be understood that the above description is intended to be
15 illustrative and not restrictive. Many embodiments will be apparent to those of skill in the art upon reading the above description. The scope of the invention should therefore be determined not with reference to the above description alone, but should be determined with reference to the claims and the full scope of equivalents to which such claims are entitled.

20 **[0155]** When introducing elements of the present invention or an embodiment thereof, the articles "a", "an", "the" and "said" are intended to mean that there are one or more of the elements. The terms "comprising", "including" and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements.

25 **[0156]** The recitation of numerical ranges by endpoints includes all numbers subsumed within that range. For example, a range described as being between 1 and 5 includes 1, 1.6, 2, 2.8, 3, 3.2, 4, 4.75, and 5.